PREDICTING CONTAMINANT TRANSPORT PATHWAYS IN THE CARIBOU-POKER CREEK RESEARCH WATERSHED

By

Vincent Autier

RECOMMENDED:

Advisory Committee Chair

Department Head

APPROVED:

Dean, College of Science, Engineering, and Mathemathics

Dean of the Graduate School

1-6-03

Date

PREDICTING CONTAMINANT TRANSPORT PATHWAYS IN THE CARIBOU-POKER CREEK RESEARCH WATERSHED

A

THESIS

Presented to the Faculty

of the University of Alaska Fairbanks

in Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

By

Vincent Autier, B.S.

Fairbanks, Alaska

December 2002

ABSTRACT

In order to evaluate the impact of natural organic matter (NOM) on drinking water, the hydrology of the Caribou-Poker Creeks Research Watershed (CPCRW) was considered. The CPCRW provided an excellent opportunity to investigate contaminant transport as it relates to hydrology in a well studied, discontinuous permafrost environment. The seasonal variation of organic chemistry of three different water sources (i.e. ground water, artesian spring and stream) was studied during the course of the year 2001.

This thesis comprises three chapters, each of which seeks to gain a better understanding of the contaminant transport pathways in a boreal watershed, Caribou-Poker Creeks Research Watershed. The hypothesis of Chapter One was that the heavy metal Cadmium (Cd) is strongly correlated to NOM. The objective was to establish the likely sources of cadmium mobility in organic rich soils. Cadmium was selected because of its tendency to be more mobile in soils than other heavy metals. The hypothesis of Chapter Two was as follows; the chemical nature of dissolved organic matter (DOM) changes during the course of a year in a boreal watershed. The objective of this study was to evaluate the seasonal character of DOM in the CPCRW. DOM was characterized using pyrolysis-gas chromatograph/mass spectrometry (Py-GC/MS), as well as ultraviolet absorbance at 254 nanometers (UV_{254}) and dissolved organic carbon (DOC). Finally, Chapter Three had for central hypothesis that water could be traced to its origin through a correlation of NOM fingerprints. NOM was used as a natural tracer. One hypothesis was that the water appearing on the discharge areas (north-facing slopes) was derived from infiltration at higher elevation on recharging area (south-acing slopes).

It was also expected to find that surface water in downstream segments could be correlated with an upstream source, and that this relationship would change during the course of the year. The main objective of this thesis was to establish the relationship of NOM type (chemical/physical characteristic) to Cd mobilization.

TABLE OF CONTENTS

CONTENT **Page**

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

CHAPTER 3

ABBREVIATIONS

A =	Absorption
AA =	Atomic Absorption
AH =	Aromatic Hydrocarbon
Al^{3+} =	Aluminium ion
AOM =	Aquagenic Organic Matter
Cd =	Cadmium
Cd^{2+} =	Cadmium ion
$CdCl_2$ =	Cadmium Chloride
$Cd(NO_3)_2$ =	Cadmium Nitrate
$Cd(OH)_2$ =	Cadmium Hydroxide
$CdSO_4$ =	Cadmium sulfate
CPCRW =	Caribou Poker Creek Research Watershed
Cr =	Chromium
Cu =	Copper
CU =	Color Units
DOC =	Dissolved Organic Carbon
EC =	Electrical Conductivity
EI =	Electron Impact
GC/MS =	Gas Chromatograph/Mass Spectrometer
GFAA =	Graphite Furnace Atomic Absorption
H^+ =	Hydrogen ion
HNO_3 =	Nitric acid

L =	Lipids
LOI =	Lost On Ignition
LTER =	Long Term Ecological Research
MCL =	Maximum Contaminant Level
N =	North
NaOH =	Sodium Hydroxide
NFPA =	National Fire Protection Association
Ni =	Nickel
NOM =	Natural Organic Matter
OH^- =	Hydroxyl ion
P =	Polysaccharides
pass =	Passing
Pb =	Lead
PCA =	Polycarboxyllic acids
POM =	Pedogenic Organic Matter
Pr =	Proteins
rem =	Remaining
RO =	Reverse Osmosis
RT =	Retention Time
SOM =	Soil Organic Matter
SS =	Stock Solution
TOC =	Total Organic Carbon
UAF =	University of Alaska, Fairbanks
UV =	Ultra Violet

W = West

W = Water

Zn = Zinc

NOMENCLATURE

b =	Langmuir's parameter
Ce =	equilibrium concentration of contaminant in the fluid
C_T =	total concentration
Ksp =	solubility product
M_T =	total mass of soil
M_S =	mass of dry soil
M_W =	mass of water
Q =	flow
q_e =	mass of sorbed contaminant per mass of sorbent
q_{max} =	maximum mass of sorbed contaminant per mass of sorbent
S =	solubility
T =	temperature
λ =	wavelength

UNITS

°C	=	degrees Celsius
cm	=	centimeters
g	=	grams
ha	=	hectares
°K	=	degrees Kelvin
kg	=	kilograms
L	=	liters
M	=	mole
mg	=	milligrams
min	=	minutes
m^3	=	cubic meters
ng	=	nanograms
nm	=	nanometers
ppb	=	parts per billion
ppm	=	parts per million
yr	=	year
µg	=	micrograms
µm	=	micrometers

ACKNOWLEDGEMENTS

I would like to thank Dr. Daniel White, my major advisor, for is perpetual support, patience and encouragement through out this research. His guidance, advice and trust in my abilities made the completion of this study easier and more bearable. The time that he gave regarding papers writing, data interpretation, or simple listening of some of my concerns was of tremendous help. Grateful thanks are extended to my advisory committee, Dr. Robert Carlson and Dr. Hajo Eicken for their support and suggestions. Special thanks to Kenji Yoshikawa, who helped me considerably with fieldwork and understanding data, but also who help me taking broader decision.

I wish to thank Sarah Garland for her help in the laboratory, running soil and water samples in the py-GC/MS. I also want to thank every individual who has been helping me, without considering time or difficulty. Everyone has been helpful in the water environmental engineering department at a time or an other. Special thanks to my numerous office mates, Timur Aitimbetov, Sarah Seelen, Corianne Hart, and Ipshita Majhi.

I also would like to acknowledge Experimental Program to Simulate Competitive Research (EPSCoR) and the Institute of Northern Engineering (INE) for the funding of this study.

And finally, I want to thank my girlfriend Vladislava Mitsik for her continual support, tolerance and patience through out this research.

CHAPTER 1. Factors affecting cadmium mobility in a boreal soil[1]

Abstract - The objective of this research was to establish likely sources of Cadmium (Cd) mobility in organic rich soils. Cadmium was selected because of its tendency to be more mobile in soils than other heavy metals, including Pb and Cu. Three soil horizons were collected from the Caribou-Poker Creeks Research Watershed, near Fairbanks, Alaska. A dilute cadmium solution was added to the soil and then the soil was size fractionated. Samples were analyzed by atomic absorption spectroscopy (AA) to determine which particle sizes the Cadmium preferred to bind. For each size fraction, natural organic matter (NOM) was analyzed by pyrolysis-gas chromatograph/mass spectrometer (py-GC/MS) to determine the nature of the NOM most responsible for Cd sorption. Results suggested that total Cd and total solids were distributed almost equally among the particle sizes in each horizon. On the other hand, the total Cd and NOM were not distributed evenly among particle sizes. Based on py-GC/MS analysis, polysaccharide (sugar) compounds were positively correlated to Cd distribution in the particle size range tested (i.e., 0.3-75μm).

[1] This is a paper in preparation to be submitted as Autier and White, "Factors affecting cadmium mobility in boreal soil" to Water Research

INTRODUCTION

Health Risks of Cadmium

Soil concentration of most metals, especially Nickel (Ni), Chromium (Cr), and Cadmium has increased over the last 60 years (Alloway, 1990; Naidu et al, 1997). The environmental hazards and health concerns derived from the heavy metals into soils are noteworthy to our society. Cadmium, for example, is toxic to humans at very low concentrations (Flick et al., 1971).

Cadmium was used for the study because of the health effects it causes if consumed in sufficient quantities and its ubiquity in drinking water, food, and air. Drinking water with very high levels severely irritates the stomach, leading to vomiting and diarrhea (Naidu, 1997). Long-term exposure to lower levels of cadmium in air, food, or water leads to a chronic accumulation of cadmium in the kidneys and disfunction if the concentration in the kidney cortex exceeds 200mg/kg (Fassett, 1980). The World Health Organization (WHO) recommended maximum intake of Cd as 70μg/day (Fassett, 1980). Other potential long-term effects are lung damage and fragile bones.

Sources

Cadmium enters the environment as a result of both natural and anthropogenic activities. It is believed that Cd in Alaskan soil is mostly derived from natural sources, such as parent rock decay, dust storms, volcanic eruptions, and forest fires. Volcanic dust was deposited in the Fairbanks area as a result of the 1912 and 1989 eruptions of Mt. Katmai and Redoubt, respectively (Beget, 2002). Some of this material remains in the soil. Also, there are about 40 major tephra layers (layers deposited from volcano eruption) in the loess around Fairbanks, some of them as much as 20-30 cm thick. Most

of these tephras are more than 100,000 years old, and so lie at depths of several meters or more. However, depending on local erosion and redeposition, the tephra layers can continue to be a source of cadmium in regional soils.

The dynamic equilibrium between Cd in the soil solution and that sorbed on the solid phase of the soil depends on the pH, the chemical nature of the metal species, the stability of Cd complexes, the binding power of the functional groups, and the ionic strength of solutions and competing ions (Pickering, 1980). The goal of this study was to investigate the binding of Cd onto different particle size fractions to help in understanding its mobility.

MATERIALS AND METHODS

Field Sampling

The soil used in this study was collected from the Caribou-Poker Creeks Research Watershed (CPCRW), near Fairbanks, Alaska, 65°10'N, 147° 30'W, 06/2001. The CPCRW is an important component of the Bonanza Creek Long Term Ecological Research (LTER) Program. A primary task of the LTER is to maintain reliable meteorological and hydrological measurements for use by scientists worldwide. In addition, process studies on the interactions between permafrost and regional hydrology and meteorology are being conducted. The CPCRW is dominated by discontinuous permafrost and has bedrock of highly fractured schist (Collins, 1986). The Caribou-Poker Creeks Research Watershed is entirely underlained by the Yukon-Tanana metamorphic complex (Ray, 1988). Chapman et al. (1971) described the complex in the watershed as

a greenschist facies, dominated by chlorotic and quartz-mica schists, with some micaceous quartzites, garnet-mica schists, phyllites, and possible greenstone or impure marbles.

The soil was collected by digging a soil pit and collecting the individual soil horizons to a depth of approximately 25 cm. The materials collected represented an OAe horizon with a thickness of approximately 12 cm, an AEv horizon with a thickness of approximately 8 cm and BE horizon collected from a depth between 20 and 25 cm (Brady, 1999). Soil horizons were separated in the field and transported to the laboratory in 20 liter coolers where they were stored at 4 °C.

Sorption Isotherms

The objective of the isotherm experiment was to determine the equilibrium sorption capacity of the soil. All samples were homogenized, air-dried, and sieved through a 1 mm mesh screen. The material passing the 1 mm mesh screen was not further disintegration with an ultrasonic device or resuspended in a blender. The sample passing through the 1 mm mesh screen was considered to be stable aggregate, and the particle size of the aggregate was the aggregate itself. Therefore, it was believed that the sorption of the Cd was on the aggregate itself, which was possibly composed of different particles. 500 mg of dry soil sample was then added to 20 mL of an aqueous solution of cadmium nitrate ($Cd(NO_3)_2$) containing 0.4, 0.8, 2, 4, 10, 20, and 40 mg Cd/kg dry soil. The pH of all the samples was set at 7±0.1 by adding either NaOH as a base or HNO_3 as an acid. The solutions were agitated for 72 Hours on a Eberback shaking table at 120 revolutions per minute (rpm), in a room held at 20 ±1 °C to reach equilibrium. Sorption of Cd to soil is normally rapid with more than 90% occurring within the first 10 minutes (Christensen, 1984)

Soil Digestions

Following the equilibration, the samples were filtered through a 0.45 μm glass fiber filter to separate the soil from the solution. The soil retained on the filter was transferred to an Erlenmeyer flask and acidified to pH less than 2 by 10 ml of concentrated (15 Molar) nitric acid solution (HNO_3). The total volume was further increased to 100 mL with metal free water. The samples were then heated on hot plates to reduce the volume to 20 ml. By doing so, the cadmium sorbed by the soil was released into the acidic solution. The concentrate was filtered through a 0.45 μm glass fiber filter into a 100 mL volumetric flask and diluted to 100 mL. The concentration of cadmium was then analyzed by atomic absorption spectrometry.

Atomic Absorption (AA)

A Perkin Elmer AA analyst 300 HGA 850 graphite furnace AA (GFAA) was used to determine the Cd content for each sample. A total of 2 mL of concentrated acid from the soil/water digestion was pipetted into the GFAA auto sampler. The sample was then introduced into an electrically heated graphite tube. The electro thermal vaporization atomized the entire sample and retained the atomized sample in the light path of 228.8 nm wavelength. The instrument was operated with a detection limit for Cd between 1 ppb and 20 ppb.

Particle Size Separation

For each of the three soil horizons, 50 g of wet soil was added to 2 L of an aqueous solution containing 50 μg/L of Cd and metal free water. The soil solutions were adjusted

to a pH of 7±0.1 by adding either NaOH or HNO_3. The samples were then agitated for 48 hours on a Eberback shaking table at 120 revolutions per minute (rpm), in a room held at 20 ±1 °C. After coming to equilibrium, the sample was filtered through 2 different filters in series (75 μm sieve & 0.3 μm glass fiber filter). Sub-samples of the material remaining on and passing each filter were collected for py-GC/MS, loss on ignition, or Cd analysis. Cadmium analysis was conducted as previously described.

Solid samples collected for py-GC/MS analysis were oven-dried at 60ºC, ground, homogenized, and stored in a desiccator until analyzed by pyrolysis-GC/MS. For the liquid samples passing the 0.3 μm filter, one liter of sample was reduced to a volume of approximately 20 mL in a Buchi RE111 Rotovap vacuum evaporator at 40°C. This concentrate was poured into a 4 oz jar and oven dried at 60°C to finalize the drying. When dried, the residue was scraped free from the jar, ground to a fine powder, homogenized, and stored in a desiccator until analyzed by py-GC/MS.

Solid samples collected for determination of NOM were dried then combusted in a Sybron Thermolyne Furnatrol muffle furnace at 550°C. The loss on ignition (LOI) was used to approximate the organic matter content of the samples.

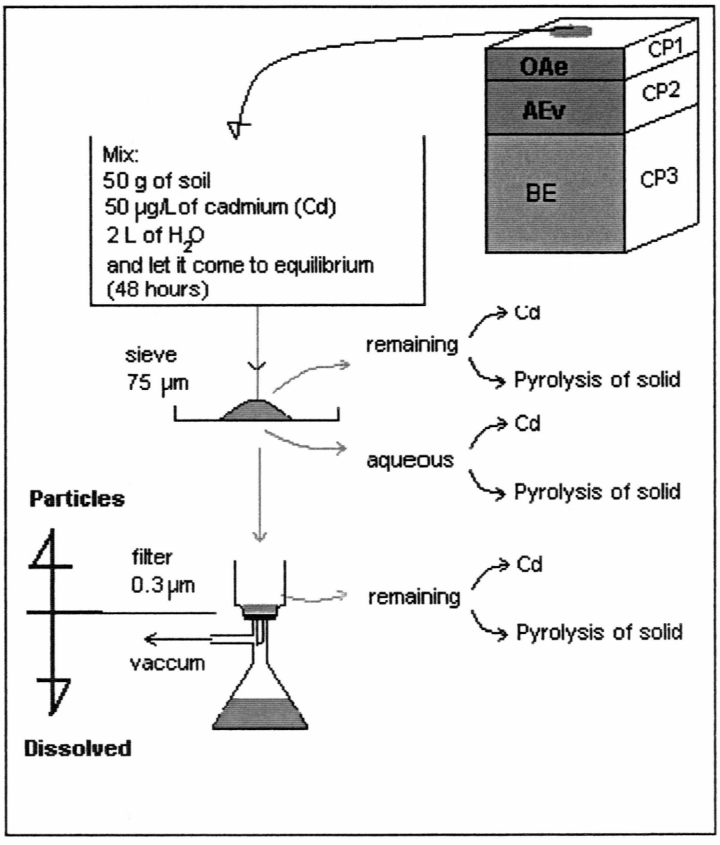


Figure 1.1 Schematic representing particle size separations.

Py-GC/MS of soil and water samples

Py-GC/MS was conducted with a CDS Pyroprobe 2000 pyrolyzer with AS2500 autosampler, mounted on an HP 6890 Gas Chromatograph with a Restek Rtx35-MS column, 30 m x 0.32 mm x 0.25 µm. Pulsed splitless injection was used, with pulse pressure at 25 psi. The pyrolysis interface and GC injection port were kept at 280°C. Before pyrolysis, the sample was held in the 280°C chamber for 15 seconds while the chamber was purged with helium carrier gas. The pyrolyzer was then switched online to the GC and pyrolysis began. The pyrolyzer temperature was ramped at 10°C/ms to 700°C and held constant for 10 seconds. After one minute, the pyrolyzer was switched

offline and column head pressure was reduced to provide constant flow of helium at 2.0 ml/min. The GC temperature program was 40°C for 30 minutes, then ramped at 1°C /min to 120°C ramp at 2°C/min to 220°C, with a final ramp at 10°C /min to 280°C and held for 10 min to clean out the column in preparation for the next sample. The GC was plumbed directly to an HP 5973 Mass Selective Detector on electron impact (EI) mode. The MS scanned mass units 45 to 350. All mass spectra were compared to the Wiley 275 spectral library.

RESULTS AND DISCUSSION

Sorption Isotherms

The natural abundance of Cd for the soils was 8.27, 10.57, and 8.87 mg/kg for the OAe and AEv, and BE horizons, respectively. The average natural abundance of Cd was higher than typical reported values of 0.22 mg/kg (Sánchez-Camazano et al., 1993). The aqueous solution of cadmium nitrate ($Cd(NO_3)_2$) used in the sorption isotherms represented between 5 and 500% of the natural abundance for all horizons.

The Langmuir isotherm describes the equilibrium relationship between the mass of sorbed contaminant per mass of sorbent (q_e) in mg/kg and the equilibrium concentration of contaminant in the fluid (C_e) in mg/l according to Equation 1.

$$q_e = q_{\max} \frac{bC_e}{1 + bC_e} \qquad \text{Eq. 1}$$

The experimental data was plotted with C_e/q_e on the *y*-axis and C_e on the *x*-axis according to Equation 2.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \qquad \text{Eq. 2}$$

The two unknown parameters q_{max} and *b* (see table 1.1) could be determined from the slope of the line ($1/q_{max}$) and the *y*-intercept ($1/[q_{max}b]$) and from equation 2. Using equation 1, the theoretical mass of sorbed contaminant per mass of sorbent q_e and the theoretical sorption isotherm were determined (see figure 1.2).

Table 1.1 Parameter q_{max} and *b* of the Langmuir sorption isotherm equation

Soil Type	q_{max}	*b*	*equation*
OAe	1.653	4.792	y = 0.6048x + 0.1262
AEv	1.581	1.372	y = 0.6324x + 0.4611
BE	1.954	0.260	y = 0.5119x + 1.9664

The natural abundance of cadmium for the OAe, AEv, and BE horizons was, 8.27, 10.57, and 8.87 ppm, respectively. It was expected to get high equilibrium sorbed contaminant concentration *qe* (mg/kg), however *qmax* was for OAe, AEv, and BE horizons only 1.653, 1.581, and 1.954, respectively (Table 1.1). The sorption of cadmium is strongly related to pH. pH is a variable and a key factor (Alloway, et al. 1990). Cadmium can be in the samples under three forms, fixed, dissolved, and sorbed. The amount sorbed is determined by the Langmuir adsorption isotherm (Figure 1.2). It was assumed that the dissolved material passing the 0.3 μm (Figures 1.1 and 1.3a) was carrying the dissolved cadmium. The percentage of sorbed and dissolved cadmium to the total cadmium was 28.8%, 21.04%, and 29.13% for OAe, AEv, and BE horizons, respectively. A substantial amount of cadmium is therefore fixed, or precipitated. It is believed that cadmium could be found in the sample under four different states (i.e. dissolved, sorbed to organic material, fixed to minerals or/and precipitated). No precipitation was observed, however the addition of the amount of cadmium found in

three different states (i.e. dissolved, sorbed to organic material, fixed to minerals) does not equal the total cadmium in the sample.

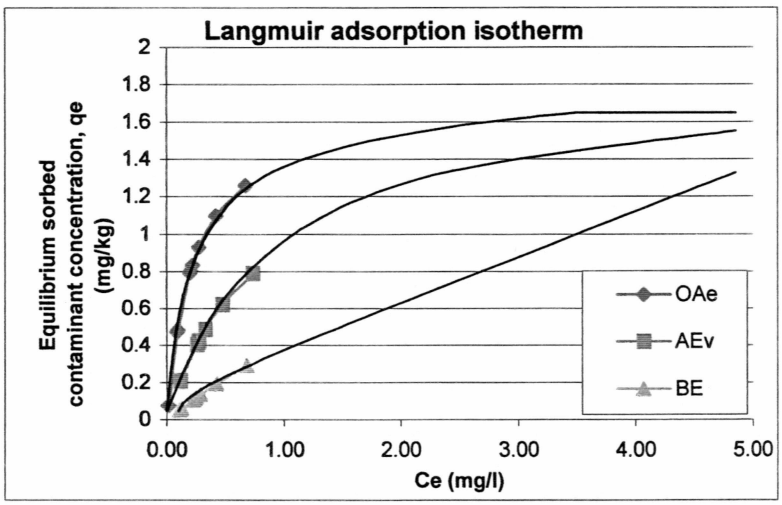


Figure 1.2 Cadmium adsorption isotherms using calculated q_e based on Equation 1.

Particle Size Separation

Figure 3 represents the Cd sorbed for the three horizons depending on the particle sizes. Each layer (OAe, AEv and BE) was run in triplicate. The plot for each layer was an average of the triplicate. The results demonstrate that the free ion Cd^{2+} was better sorbed by BE, than by AEv or OAe, for the particle size ranging between 0.3 and 75 μm (Figures 1.3-a and 1.3-d). Figure 1.3-a illustrates a larger percentage (84%) of cadmium sorbed by BE in the 0.3-75 μm range. Also figure 1.3-d displays the mass of cadmium sorbed per mass of OM in the range 0.3-75 μm. The mass of Cd sorbed by BE, OAe, and AEv was 118.9, 74.3, and 71.9 μg Cd/ g OM respectively. Higher amounts of Cd being sorbed by BE is contradictory with Page (1987). In the Page study, histosols contained most of the Cd. Histosols have primarily organic content. Here, the BE horizon contained the least amount of organic matter with only 6% in the range 0.3-75 μm. However, the BE horizon sorbed the larger amount of Cd.

Sorption is a surface phenomenon in which chemical species adhere to an interface. Therefore, it was expected to find more cadmium sorbed by smaller size components of the soil, as dissolved compounds (Mayer, 1994 a, b). Yet, the percentage of Cd sorbed on the dissolved particles accounted for only 6-7%. For particle sizes greater than 0.3 μm, 93-94% of the Cd was sorbed. Between 66-84% of the Cd was sorbed to the particles ranging in size between 0.3 and 75 μm, for OAe and BE respectively. Comparing figure 1.3-a to figure 1.3-b, the relative Cd distribution appeared to be most influenced by the solids distribution. This result suggests that the Cd sorbed equally well to solids in the size range 0.3 – 75 μm as that greater than 75 μm. The Cd and solids distribution were on a mass basis, suggesting that the relative surface area available for sorption was either equal among all particles or played a minor role in the sorption for this soil.

Most of the organic matter (≈80%) in all horizons were present as particles larger than 75 μm (Figure 1.3-c). However, even though organic matter (OM) particles larger than 75 μm were more abundant than OM particles ranging between 0.3-75 μm, Cd largely preferred bounding with smaller OM size (Figure 1.3-d).

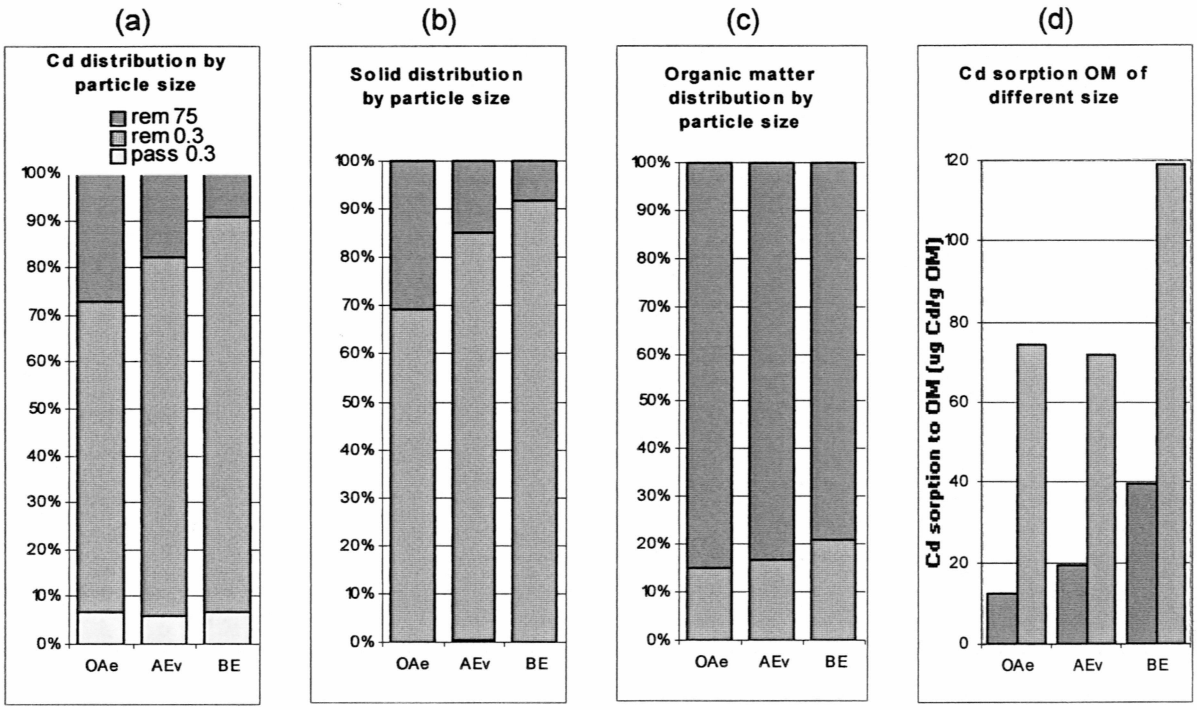


Figure 1.3 (a) Cadmium sorbed as a function of particle size and soil type; (b) Solid distribution as a function of particles size and soil type, (c) organic matter distribution as a function of particles size and soil type, (d) Mass of sorbed Cd per mass of organic matter as a function of particles size.

Figure 4 represents the percentage of cadmium found on each horizon/size range versus the percentage of solids attributable to each horizon/size range, and versus the percentage OM distribution for different particles for the three horizons. Each layer (OAe, AEv and BE) was run in triplicate. The average of the triplicate was plotted for each horizon and each size range. Correlation was plotted for each size range. As seen in Figure 4-a, a strong linear relationship (i.e. $r^2 = 0.97$ for solids remaining on 0.3 µm and $r^2 = 0.96$ for solids remaining on 75 µm) existed between the percentage of Cd found on each horizon/size range and the percent of total solids retained on each horizon/size range. Therefore the Cd found on each horizon/size range appeared to be independent of particle size. It is believed that this relation is due to the low density of the soil

remaining on the 75 µm filter. On a per mass basis, less solid remained on the 75 µm filter than on the 0.3 µm filter. However, these solids had a higher content of OM (i.e. 58% against 11%) regardless of the horizon. In general, OM has a lower density than minerals. In addition, the Cd seemed to have a higher infinity for OM (Figure 1.4-b).

As shown in Figure 4-b when the OM distribution (%) increased, the Cd found on each horizon for particles remaining on the 75 µm sieve increased. The correlation between Cd found on each horizon for particles remaining on the 75 µm sieve and OM distribution was equal to 0.95. The same behavior could be seen for particles remaining on 0.3 µm filter, (Figure 1.4-b). The correlation between the Cd found on each horizon for particles remaining on the 0.3 µm sieve and the OM distribution was equal to 0.94. Cd distribution was well correlated to OM distribution. However, the apparent relationship between Cd and OM may be an artifact of the solids distribution. In all three soil horizons, the proportion of OM retained on each sieve increased with the proportion of total solids retained (see Figure 1.3-b and c).

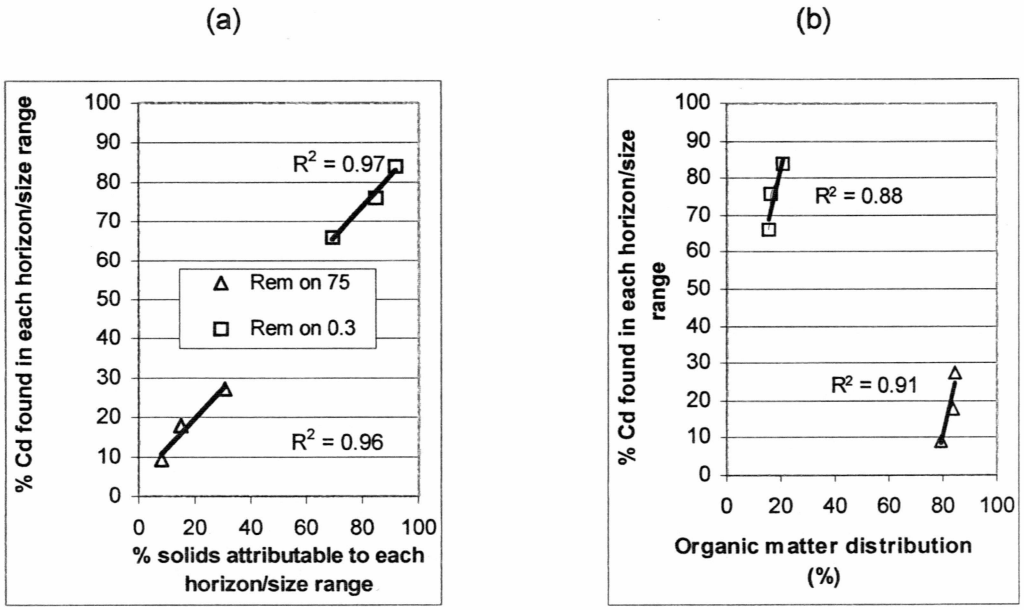


Figure 1.4 (a) Cd distribution versus solid distribution for particles remaining on 75μm and 0.3 μm sieves; (b) Cd distribution versus organic matter distribution for particles remaining on sieve 75μm and on sieve 0.3μm

Pyrolysis Results

Zakaria M., 2001, found that the capsular polysaccharides, main constituent of the Cyanobacterial envelope, adsorbed high amounts of both Cd^{2+} and Mn^{2+}. Polysaccharides have the ability to adsorb Cd^{2+}. Figure 3-a suggests that 6% of cadmium was sorbed to materials passing 0.3 μm. The material passing 0.3 μm, is defined as dissolved, in contrast, the material remaining on this size filter is defined as particulates (Buffle, 1990). It was assumed that the dissolved materials passing through the 0.3 μm filter were available for transport. Since the materials passing through 0.3 μm contained only 25.82 % (Figure 1.5) of polysaccharides in comparison to stream, groundwater and spring, which contain respectively 49.30%, 47.72%, and 36.84%. The data suggests that stream, groundwater, and spring of the boreal watershed CPCRW have the potential to mobilize the heavy metal, cadmium.

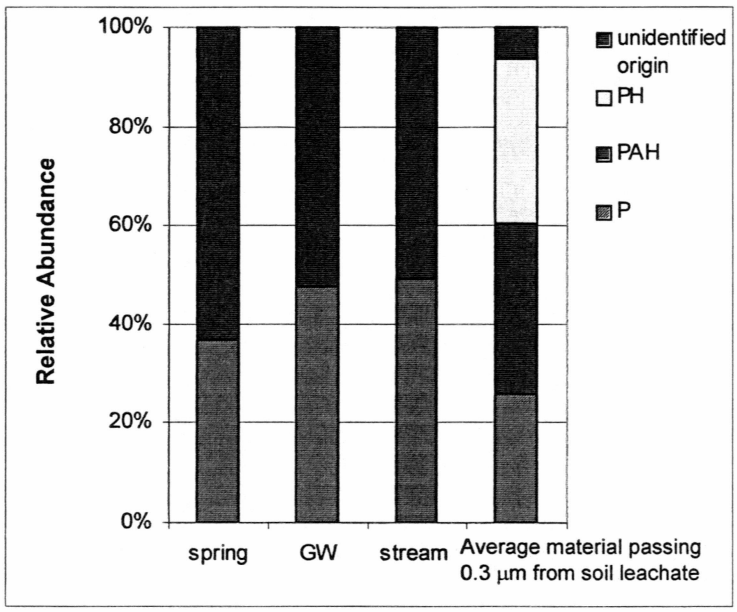


Figure 1.5 Potential for stream, spring and ground water to transport the heavy metal, Cadmium, into the water system. Phenol, PH; poly-aromatic hydrocarbon, PAH; polysaccharides, P

Transphilic acids contain a higher concentration of sugars and amino sugars, represented in chromatograms as furans, furfurals (Croue et al., 2000). Thus, furfural and 2-furancarboxaldehyde 5-methyl are polysaccharide products. Therefore, those two compounds contributed to the Cd distribution. From figure 1.6-a, polysaccharides were correlated to the mass of OM by correlation factors of 0.99 for furfural and 0.96 for 2-furancarboxaldehyde 5-methyl. This suggested that the amount of polysaccharides is in direct relation with the amount of OM. However, care should be taken with the correlation, due to a low gradient (Figures 1.6-a and b). BE horizon had less OM than AEv and OAe horizons; therefore, BE had a lesser amount of polysaccharides (Figure 1.6-a). In addition, the percentage of Cd distribution for the OAe (similar trend to AEv and BE) was well correlated to the percentage index of the polysaccharides, with correlation factors equal to 0.98 and 0.97 for respectively 2-furancarboxaldehyde 5-

methyl and furfural. Those two polysaccharide products seemed to govern the Cd distribution (Figure 1.6-b). Only the percentage cadmium distribution of the OAe horizon (i.e. moss) was plotted against the percent index of polysaccharides, AEv and BE showing similar correlation.

Polysaccharides are in greater amount in the soil organic matter (SOM) rich soil. The percentage of SOM decreased with depth due to the bacterial degradation; therefore, the amount of sugar also decreased with depth. This results in a percentage index of polysaccharides decreasing with depth. Since high amounts of Cd^{2+} sorb to polysaccharides (Zakaria, 2001), the sorbed cadmium decreased with depth (Figures 1.6-a and 1.6-b).

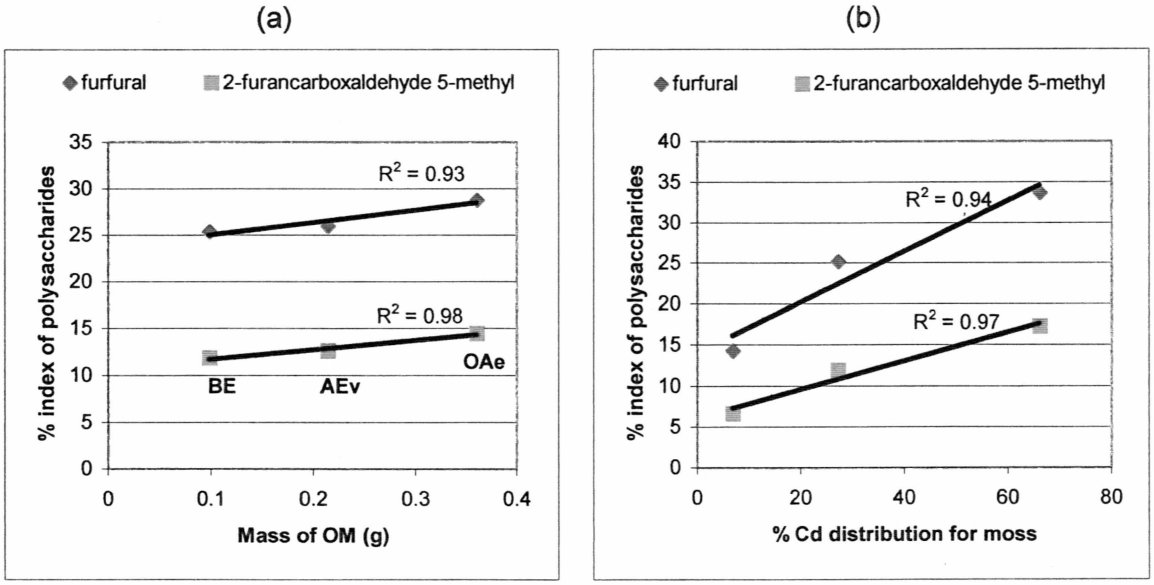


Figure 1.6 (a) Correlation between OM and Polysaccharides; (b) correlation between Cd distribution and Polysaccharides

Tables 1.2 and 1.3 represent respectively the correlation of the OAe, AEv, and BE triplicates, in relation to the particle sizes. The correlation is based on pyrolysis data. Pyrolysis is a method by which specific components of DOM can be compared to understand relative changes in chemical composition. The correlation is based on the sum of the relative abundance of the index previously chosen. Table 1.2 suggests that the material passing the filter 0.3 µm is different from the (nature and characteristic of the) material remaining on a 75 µm filter as well as that remaining on a 0.3 µm filter. However, the difference decreases as the depth increases. The correlations for the OAe (0-12cm), AEv (12-20cm), and BE (20-25cm) horizons, between the material remaining on filter 75 and passing 0.3 µm were 0.48, 0.73, and 0.89, respectively. The percentage of SOM also decreased with depth, decreasing the differences in the materials characteristics.

In addition, Table 1.3 shows that for different filter size, material passing or remaining on the filter is somewhat equivalent when correlated. Correlation factors were ranging between 0.843 and 0.998. This led us to believe that the material of each filter size would have similar chemical and physical composition.

Table 1.2 Correlation for different horizons, between different filter size

OAe	Rem-0.3	Pass-0.3
rem-75	0.91	0.48
rem-0.3		0.60

AEv	Rem-0.3	Pass-0.3
rem-75	0.91	0.73
rem-0.3		0.87

EB	Rem-0.3	Pass-0.3
rem-75	0.96	0.89
rem-0.3		0.96

Table 1.3 Correlation for different filter size, between different horizons

Rem 0.3	AEv	EB
OAe	0.90	0.84
AEv		0.99

Pass 0.3	AEv	EB
OAe	0.93	0.93
AEv		1.00

Rem 75	AEv	EB
OAe	0.92	0.85
AEv		0.96

CONCLUSION

The objective of this research was to establish likely sources of Cd mobility in organic rich soils. Results suggested that Cd^{2+} ion was better sorbed by BE horizon, than by AEv or OAe, for the particle size ranging between 0.3 and 75 μm. In addition, Cd distribution appeared to be most influenced by the solids distribution. When the amount of material increased, the amount of sorbed Cd also increased. However, these results were found on a per mass basis and might differ if the samples would have been further disintegrated (to consider particles and not stable aggregates) and/or if considering the surface area of the particles (Mayer, 1994a).

Cd distribution was well correlated to OM distribution, with correlation factors ranging between 0.95 and 0.94, respectively to particle size. Yet, care should be taken once again. OM are believed to have an affinity for mineral grain surface (Mayer, 1994b). On a surface area basis, Cd could also be coating mineral particles. Since Cd and OM would have the same affinity to mineral, the correlation would be high, however sorption to mineral particles would be the governing factor.

Croue et al. (1999), suggested that sugars (polysaccharides) were represented in chromatograph as furans and furfurals. Results showed that polysaccharide products seemed to govern the Cd distribution, due to high correlation factors (i.e. 0.98 and 0.97) between Cd distribution and polysaccharides. The amount of polysaccharides was in direct relation with the amount of OM. The percent of OM decreased with depth, going from 36.1% for OAe, to 21.4% for AEv, and finally to 9.9% for BE. This resulted in a decrease of sorbed cadmium with depth. As a limitation to the previous statements, it should be understood that polysaccharides in soil are generated through different mechanisms. One source of polysaccharide is through bacterial production or microorganism secretion (Buffle, 1990). Therefore, it is not uncommon to find polysaccharides associated with mineral fraction if the bacterium itself is attached to mineral surface. Hence, the high correlation observed between Cd and OM, could be due to the OM being the source of the polysaccharides. In a different type of soil, a high correlation between Cd, mineral, and polysaccharides could be observed.

It was assumed that the dissolved materials were available for transport. The data suggested that streams, groundwater, and springs of the boreal watershed CPCRW have the potential to mobilize the heavy metal, cadmium.

REFERENCES

1- Adriano D.C. 1986. Trace elements in the terrestial environment. Spring-Verlag, New York.

2- Alloway B.J., Environmental Science, Queen Mary and Westfield College, University of London, " Heavy Metals in Soils", John Wiley & sons, Inc, 1990

3- Alloway B.J. 1990. cadmium.p.100-124. In B.J. Alloway (ed.) Heavy metals in soils. John Wiley and sons, New York

4- Beget Jim (2002) Geology Dept, tephrochonolgy specialist, personal communication

5- Bennett, B.G., *Exposure Commitment Assessments of environmental pollutants* Vol 1., No1. MARC, London (1981)

6- Biddappa, C.C., Chino, M. and Kumazawa, K. *Plant and soil* 66 (1982) 299-316

7- Blom, E. B. *Sorption of Cadmium by soils* Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire (1974) GB 2401 C76 no 320 c.2

8- Boul, S.W., F.D. Hole, R.J. McCraken, and R.J. Southard (1997). *Soil Genesis and classification,* 4th ed (Ames, Iowa; Iowa state University press)

9- Brady N.C., Ray R. Weil (1999) The nature and properties of soils. *2-18 The soil profile* P65-69. 12th ed Prentice hall

10- Brummer, G., K.G. Tiller, U. Herms, and P.M. Clayton. 1983.*Adsorption-desorption and/or precipitation-dissolution processes of Zinc in soils.* Geoderma 31:337-354

11- Buffle J., *The components of aquatic systems and their reactivity; Complexation reactions in aquatic systems*, Ellis Hordwood (1990), 16-89, 21.

12- Chapman, R.M, F.R. Weber, and B. Taber. 1971. Preliminary geologic map of Livengood quadrangle. U.S. Geological Survey. Open File Report 483. scale 1:250,000

13- Christensen, T.H., Water, Air & Soil Pollution 21, 1984, 105-114

14- Clair N. Sawyer, Perry L. McCarty, Gene F. Parkin. *Chemistry for Environmental Engineering; Basic concepts from General Chemistry,* Mc Graw-Hill series in water resources and environmental engineering, 1994, 36-38.

15- Collins, C.M., 1986. *The installation of long term ground temperature monitoring sites in the Caribou-Poker Creeks Research Watershed.* Technical note. NH: U.S. Army Cold Region Research and Engineering Laboratory. P. 28

16- Croue, J-P., Debroux, J-F, Amy G.L. Aiken, G.R. and Leenheer J.A., 1999. *NOM: structural characteristics and reactive properties; Formation and Control of Disinfection By-Products in Drinking Water,* P.C. Singer, ed/ American Water Works Association, Denver CO, 65-89

17- David W. Rutherford, Cary T. Chiou. *Effect of water in Soil Organic Matter (SOM) Composition on the Partition of Organic Compounds,* U.S. Geological Survey, Environmental Sci. Technol. 1992, 26, 965-970.

18- Fanning, D.S., and C.B. Fanning 1989 *Soil: Morphology, Genesis, and classification* (New York, Jhon Wiley and Sons)

19- Fassett, D.W., *Metals in the Environment* ed. Waldron, H.A. Academic Press, London (1980), 61-110

20- Fleischer, M., Sarofim, A.F., Fassett, D.W., Hammond, P.Shacklette, H.T., Nisbet, I.C.T. and Epstein, S., *Environ. Health Perspect.* 7 (1974), 253-323

21- Flick, D.F., H.F. Kraybill, and J.M. Dimitroff. 1971. Toxic effects of cadmium: A review. Environ. Res. 4:71-85

22- Hutton, M. *Cadmium in the European community,* MARC Rep. No. 2., London (1982)

23- Lamy I., Bourgeois S., and Bermond A. 1993. *Soil cadmium Mobility as a Consequence of Sewage Sludge Disposal.* Environ. Qual. 22:731-737

24- Mayer L. M. (1994a) Surface area control of organic carbon accumulation in continental shelf sediments. Geochim. Cosmochim. Acta 58, 1271-1284.

25- Mayer L. M. (1994b) Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. Chem. Geol. 114, 347-363.

26- McGrath, S.P., in *Trace Substances in Environmental Health* 20 (1986) 242-252

27- Naidu R. ; Kookana, R.S Sumner. M.E. 1997. *Cadmium sorption and transport in variable charge soils.* Journal of Environmental quality v. 26 (May/June 1997) P.602-617

28- Naidu R., M.E. Sumner, and R.D. Harter. 1997. Sorption of heavy metals in strongly weathered soils: An overview. J. Environ. Geochem. Health (In press)

29- Page, AS.L., Chang, A.C., and Mohamed El-Amamy, in *Lead, Mercury, Cadmium and arsenic in the environment* SCOPE 31, eds. Hutchinson, T.C. and Meena, K.M. John Wiley, Chister (1987), 119-146

30- Pickering, W., *Cadmium in the environment. Part 1 Ecological Cycling,* ed Nriagu, J.C John Wiley, New York (1980), 365-397

31- Ray, S.R. 1988. Physical and chemical characteristics of headwater streams at Caribou-Poker Creeks Research Watershed, Alaska. Master's thesis, University of Alaska. Fairbanks, Alaska. 172 pp.

32- Sánchez-Martín M.J. and Sánchez-Camazano M. 1993. Adsorption and Mobility of Cadmium in Natural, Uncultivated Soils. Environ. Qual. 22:737-742

33- Sposito, G. and Page, A.L., in *Metal Ions in Biological Systems,* ed.Sigel, H. Marcel Dekker, New York (1984), 287-332

34- Street, J., Lindsay, W.L. and Sabey, B.R., J. *Environ. Qual.* 6 (1977), 72-77

35- Suen-Zone L., H. E. Allen, D. L. Sparks, P. F. Sanders, and W. M. Peijnenburg. 1996. Predicting Soil-Water Partition Coefficient for Cadmium. Environ. Sci. Techn. 30, 3418-3424

36- Tiller K.G. 1989. Heavy metals in soils and their environmental significance. Adv. Soil Sci. 9:113-142

37- Tills, A.R. and Alloway, B.J. *J. Soil. Sci* 34 (1983), 769-781

38- Zakaria A. M., *Removal of cadmium and manganese by a non-toxic strain of the freshwater cyanobacterium Gloeothece magna,* (2001) Water Research, Vol. 35 (18) 4405-4409.

CHAPTER 2. Seasonal variation in organic matter chemistry in a boreal watershed[1]

Abstract - The chemistry of dissolved organic matter in a watershed has a significant impact on carbon fate in the ecosystem. The objective of the research conducted herein was used to evaluate the seasonal character of natural organic matter (NOM) in the Caribou-Poker Creeks Research Watershed (CPCRW). CPCRW is an important component of the Bonanza Creek long-term ecological research (LTER) program.

The seasonal variation in true color, ultraviolet absorbance at 254 nanometers (UV_{254}), and DOC concentration for 6 different streams and 9 different springs were compared. The seasonal variation of the true color, UV_{254} and DOC showed two distinct groups. One with higher values occurring in the late summer, and the other with higher values in early summer. The research also showed that there was little difference between true color-UV_{254}-DOC relationship between spring and stream samples. However there was a significant difference in this relationship as a function of sample collection time (i.e. March, June, and August).

Using py-GC/MS, a suite of molecules was selected to look at changes in the molecular composition of DOC in CPCRW. There was a significant difference of the molecular composition of the DOC as function of season. The most pronounced difference was an abundance of nitriles and a lack of alkylbenzenes in the March pyrolyzates when compared to June and August samples. These results were expected since the nitriles are believed to be derived from proteins accumulating from microbial degradation of organics over the winter. The alkyl benzenes, believed to be derived from

[1] This chapter is in preparation for submittal as Autier, White, and Yoshikawa, "Seasonal variation in organic matter chemistry in a boreal watershed", to Water Research

decomposing lignin-rich plant material, were more abundant in the summer when material from the surface runoff enters surface water bodies.

Results from this research suggest that the organic matter abundance and molecular composition change appreciably over the course of the year.

INTRODUCTION

It was described in Chapter 1, that polysaccharides compounds would be in relation to NOM, and therefore would have the potential to bind with cadmium. In addition, Figure 6-b (Chapter 1) was suggesting that more polysaccharides would be found when the amount of NOM increase. Thus the sorption of cadmium would depend on the quality and quantity of NOM available. The main hypothesis of the Chapter 2 was that the organic matter chemistry of the boreal watershed (CPCRW) is changing with time. Variability of the characteristics and quantity of the DOM suggest that a water's potential to mobilize cadmium could change with the seasons. The objective was therefore to evaluate the seasonal character of DOM.

MATERIALS AND METHODS

Site Description

Field research was conducted in the Caribou-Poker Creeks Research Watershed (CPCRW), 48 km northeast of Fairbanks Alaska. The CPCRW is an important component of the Bonanza Creek Long Term Ecological Research (LTER) Program.

LTER maintains reliable hydrological and meteorological measurements for use of worldwide scientists. The CPCRW lies at latitude 65°10'N, longitude 147°30'W. The area is underlain by discontinuous permafrost. In general north facing and shaded slopes and valleys are underlain by permafrost with depth ranging from 10 to 50 m. South facing slopes and sites of historical forest fires may be entirely free of permafrost. In areas where permafrost has been degraded, thermokarst is a dominant feature. There are several faults that pass through the CPCRW complicating groundwater hydrology. For instance, one fault passes generally east west through the C3 watershed (Forbes and Weber, 1982). In addition, a forest fire in 1924 burned most C3 watershed, and a prescribed fire was burned in the C4 watershed in July 1999 during four days that partially burned the north-facing slope of the watershed. The CPCRW also contains two pingos, an active pingo and a collapsed pingo, adjacent to Caribou Creek.

Springs flow year-round on North and South-facing slopes. The confining layer on North-facing slopes is thought to be the permafrost itself whereas the springs flowing off South-facing slopes emerge from cracks in bedrock. Bedrock in the CPCRW is predominantly schist that is highly fractured and weathered (Collins, 1986). The origin of groundwater emerging from the springs on North-facing slopes is thought to be derived from water infiltrating higher in elevation on the South-facing, permafrost free slopes outside the topographic watershed boundaries (Lawson et al, 1991).

Sampling in the field

Samples were collected during 2001 in March (winter season: minimal water flow in streams, frozen active layer), June (spring break up: approximately 9 months of accumulated precipitation was thawing as well as the ground, and August (thawed

ground, summer rain fall). The dates of sampling events are shown in Figure 2.1. In total, 9 springs and 6 streams were sampled (Figure 2.2).

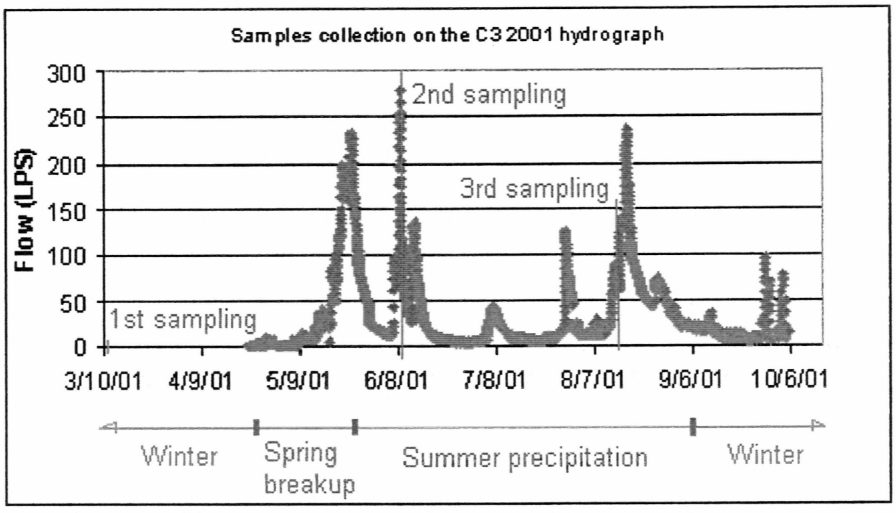


Figure 2.1 Sampling periods in accordance to the C3 2001 hydrograph

Spring samples were collected using a 60 ml syringe to draw 4 liters of water from clear flowing water at the point the spring emerges. Stream samples were collected as grab samples from below the water surface. For all samples, 4 liters of water were collected, using 1-liter amber glass bottles. The conductivity and temperature of the water samples were determined *in situ*. The bottles were then set in a cooler and brought back to the UAF laboratories where additional tests were performed. The glass bottles were stored in a refrigerator at 4°C.

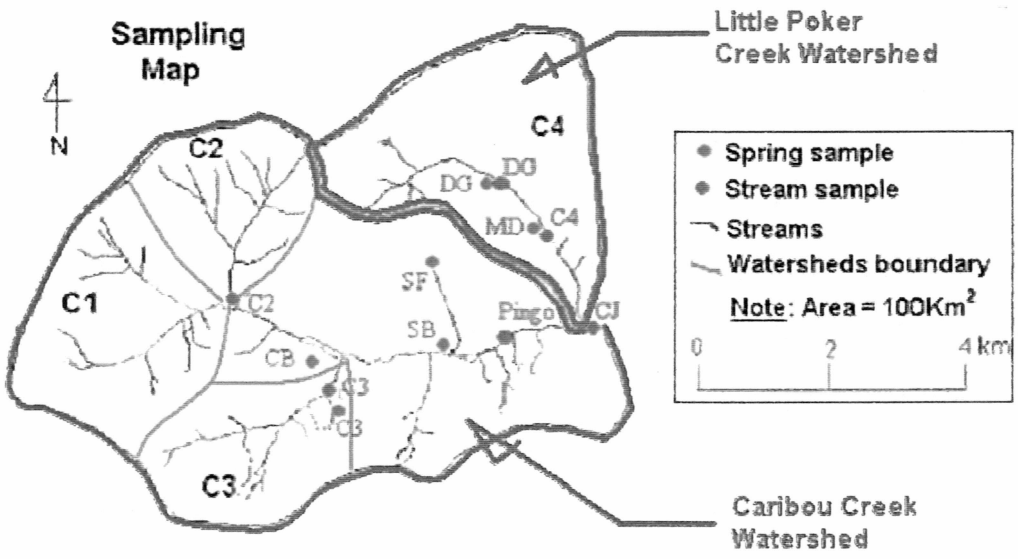


Figure 2.2 Sampling map of different water sources in the CPCRW

The simplest method used to characterize NOM is organic carbon concentration in mg/L, either as TOC or DOC, or by UV absorbance at 254 nm (UV_{254}). Another method used to characterize NOM was pyrolysis gas-chromatograph/mass spectrometer (py-GC/MS). This method made it possible to differentiate chemical characteristics of NOM.

Water Analysis

Color

Apparent color and true color were determined using an Orbeco-Hellige 975 MP Water Analysis System according to Standard Method 21020B.3 (Clesceri et al. 1998). Apparent color is a measure of the absorbance of water at 460 nm before filtering it on a 0.45 μm glass fiber filter. The true color is the same measure after filtering the sample. Each sample was compared to a "blank" of distilled water. The color experiment is done at room temperature (20±1°C).

UV-254

Ultra violet absorbance at 254nm was determined using the Ultra Violet spectrophotometer Beckman DU 520. The experiment was done after filtering the sample on a 0.45μm glass fiber filter and at room temperature (20±1°C).

The blank was prepared by using a quartz cell, which was first washed with Beckman trace-clean solution and then rinsed with reverse osmosis (RO) water. Distilled water was used as blank. The surfaces of the cell were cleaned with wet and dried wiper. The wavelength λ was set at 254 nm. The blank absorbance (1/cm) was determined and set as zero by the instrument. Each sample was compared to the blank. The instrument analyzes the UV_{254} by looking at the difference between the blank and the sample. The absorbance was measured in duplicate with a variation coefficient less than 2%.

DOC

The Total Organic Carbon Analyzer Shimadzu TOC-5000A was used to determine the concentration of dissolved organic carbon (DOC). The water samples were filtered on a 0.45 μm glass fiber filter to separate dissolved components from suspended particles. Water samples were poured in 10 ml test tubes, and then acidified with 100 μl of hydrochloric acid (HCl) to decrease the pH below 2 and purged to remove carbon dioxide. Each sample was recorded, labeled, and introduced into the auto-sampler. Four standard concentration of DOC (1, 5, 10 and 20mg/l) were created as a calibration curve prior starting the analysis. The percentage error was checked, introducing sparsely into

the auto-sampler some control test tubes, as blank, known amount of DOC; and a few identical samples.

Pyrolysis-GC/MS

Samples where filtered at 0.3 μm on a glass fiber filter and refrigerated at 4°C until analyzed. Two liters of each sample were dried in a Büchi RE-111 Rotovap vacuum evaporator at 40°C to a volume of approximately 20mL. This concentrate was poured into a 4oz jar and placed in a drying oven at 60°C to finalize the drying. When dry, the residue was scraped free from the jar, ground to a fine powder with a stainless steel spatula, homogenized and stored in a desiccator until analyzed by py-GC/MS. A portion of the powder, equal to the yield from approximately 0.5mg of DOC, was placed in a quartz sample tube for pyrolysis. (Each sample tube was injected with an internal standard consisting of 0.4μg of poly-α-methylstyrene in 4 μl of methylene chloride).

Pyrolysis-GC/MS was conducted with a CDS Pyroprobe 2000 pyrolyzer with AS2500 autosampler, mounted on an HP 6890 Gas Chromatograph with a Restek Rtx35-MS column, 30 m x 0.32 mm x 0.25 μm. Pulsed splitless injection was used, with pulse pressure 25 psi. The pyrolysis interface and GC injection port were kept at 280°C. Before pyrolysis, the sample was held in the 280°C chamber for 15 seconds while the chamber was purged with helium carrier gas. The pyrolyzer was then switched online to the GC and pyrolysis began. The pyrolyzer temperature was ramped at 10°C/ms to 700°C and held constant for 10 seconds. After one minute, the pyrolyzer was switched offline and column head pressure was reduced to provide constant flow of helium at 2.0 ml/min. The GC temperature program was 40°C for 30 minutes, then ramp at 1°C /min to

120°C. A final ramp at 10°C /min to 280°C and hold for 10 min was used to clean out the column in preparation for the next sample. The GC was plumbed directly to an HP 5973 Mass Selective Detector on electron impact (EI) mode. The MS scanned mass units 45 to 350. All mass spectra were compared to the Wiley 275 spectral library.

Table 2.1 Selected pyrolysis products or index (PCA = polycarboxylic acids, PAH = poly-aromatic hydrocarbon, P = polysaccharides, L =lipids, Pr = proteins).

#	*Compound*	*Possible origin*
1	dimethyl benzene	PAH
2	furfural	P
3	methyl cyclopentenone	PCA
4	trimethyl benzene	PAH
5	benzaldehyde	
6	benzofuran	P
7	benzonitrile	Pr
8	phenyl ethanone	
9	methyl benzonitrile	Pr
10	Azulene	L
11	2-methyl Naphtalene	L

Following the pyrolysis of NOM, a complex chromatograph is generated; generally called fingerprint. The chromatograph represents the abundance of each compound of the NOM versus time. An index (suite of compounds) of 11 compounds was selected (Table 1-1). It is important to note that those compounds were the results of pyrolysis and are not necessarily found as such in the water. HP Chemstation software was used to extract and integrate ion chromatograms of the most abundant ion of each compounds of the index.

RESULTS AND DISCUSSION

Conductivity

Conductivity measures water's ability to conduct an electric current and is directly related to the total dissolved solids in the water. Dissolved solids typically include ions such as bicarbonate, sulfate, chloride, calcium, magnesium, sodium, potassium, and phosphate (Fedeler, 2001). In general, water that percolates deep in the subsurface has a greater opportunity to dissolve minerals and increase in conductivity. Surface runoff, on the other hand, is typically free in minerals and therefore has a low conductivity.

In March, when the streams at CPCRW are fed by groundwater, conductivities of all streams and springs should be similar. As shown in Figure 2.3, the average conductivies of streams and springs are closely related for the March sampling period. The fact that the average conductivity of stream samples was somewhat lower than the spring samples could be attributed to the fact that some snow, melted by the streams, contributed to lower stream conductivity.

An increase in the average conductivity of spring waters in the June sampling period, compared to March and August was unexpected. If springs were affected by rapid infiltration of summer precipitation, a decrease in the conductivity would have occurred in June. Rather than the June conductivity being an increase over the March and August samples, however, it is believed that the conductivity of the March and August samples were lowered by snowmelt or precipitation in the emergence zone. Snow has generally a lower dielectric conductivity than water (Leya et al., 2000). When a spring emerges through ice and snow it will invariably incorporate some melt water, lowering the

conductivity. Evidence of precipitation contaminating a stream is shown by DG spring in Figure 2.3, which has an exceptionally low conductivity in August.

The average stream conductivity decreased from March to June to August. This result was expected since the streams gradually gained runoff during the course of the summer. The contribution of high conductivity base flow diminished from March to August. If the actual conductivity of the springs, on a year-round basis, were 160 μS/cm (as indicated by the June samples) then the contribution to streams by base flow could be calculated as 72% in March, 56% in June and 47% in August. This calculation is limited by the fact that the springs have different conductivities and the spring flow rate and conductivity has no relation to the relative amount of base flow entering the stream system. The calculation assumes that each spring is representative of an equal amount of base flow entering the stream.

The conductivity of the individual springs in the Caribou Creek watershed (i.e. SB, CB, C3) was higher than the conductivity of the springs in the Little Poker Creek watershed (i.e. MD and DG springs). However, the streams in the Caribou Creek watershed (C2, C3) had a lower conductivity than streams in the Little Poker Creek Watershed (C4, DG). This result suggests that base flow was a much more important source of stream water in the Little Poker Creek watershed than in the Caribou Creek watershed. This was further shown by the seasonal trend in conductivity. During the course of the season, the conductivity in the Caribou Creek streams dropped dramatically while the conductivity in the Little Poker Creek streams remained relatively constant. This result may be in part due to the impact of the relative permafrost coverage in the respective watersheds. The CJ stream is the combined flow of Caribou Creek and Little Poker Creek. Based on conductivity, the stream sample reflects most closely the

Caribou Creek streams. This was expected since the flow rate of Caribou Creek is 3 times greater than Little Poker Creek.

The pingo spring and stream were considered separately since it was believed to be derived from a unique source of groundwater, perhaps related to a fault line passing trough the watershed (White et al., 2002).

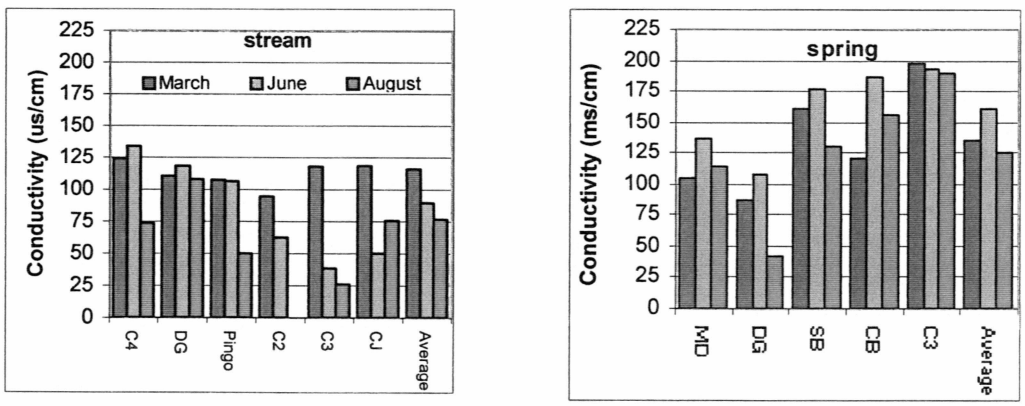


Figure 2.3 Evolution of the conductivity for each site.

Color, UV absorbance and DOC

True color, UV-254 absorption, and DOC are techniques used to measure water quality. In this research these techniques exhibited similar trend. Figure 2.4 represents the seasonal variation of OM only through the UV-254 absorbance and DOC (true color being similar).

In regards to the true color, UV-254 absorption, and DOC of streams (Figure 2.4), Little Poker Creek streams (C4, DG) increased continuously from March to August. On the other hand, Caribou Creek steams (C2, C3) exhibited a dramatic increase between March and June and then a decrease between June and August. As expected from the conductivity data, the pattern in the organic matter parameters in the CJ stream behaved

more like Caribou Creek than Little Poker Creek. Also not unexpected, pingo stream did not exhibit the same behavior as other Caribou Creek streams.

One hypothesis to explain the different seasonal behavior in the organic matter between the Caribou Creek and Little Poker Creek watersheds is the difference in permafrost coverage. Approximately 27% of the Caribou Creek watershed is underlain by permafrost whereas only 18% of the Little Poker Creek watershed is underlain by permafrost. Greater permafrost coverage corresponds to a greater runoff/infiltration ratio. A system with greater runoff could result in an earlier purging of leachable organic matter. No patterns were observed in the organic matter content of springs as were observed for streams. This was not unexpected since spring water in CPCRW likely resided in the ground 5-30 years (Yoshikawa, unpublished data).

As shown in Figure 4, springs exhibited different fluctuations in the organic matter parameters measured than streams. In general, the increase in NOM for springs appeared later in the summer. This is believed to be derived from the thickness of the active layer regulating the intra-flow. Conceptually the active layer was at its maximum thickness in winter (i.e. March), springs were fed only by baseflow (i.e. DOC = 0.9 mg/L). In June the active layer was receding allowing some intra-flow and baseflow to mix at the right of the spring (i.e. DOC = 2.5 mg/L). Later in the season (i.e. August) the active layer was fully unfrozen, giving rise to maximum intra-flow (i.e. DOC = 5.1 mg/L).

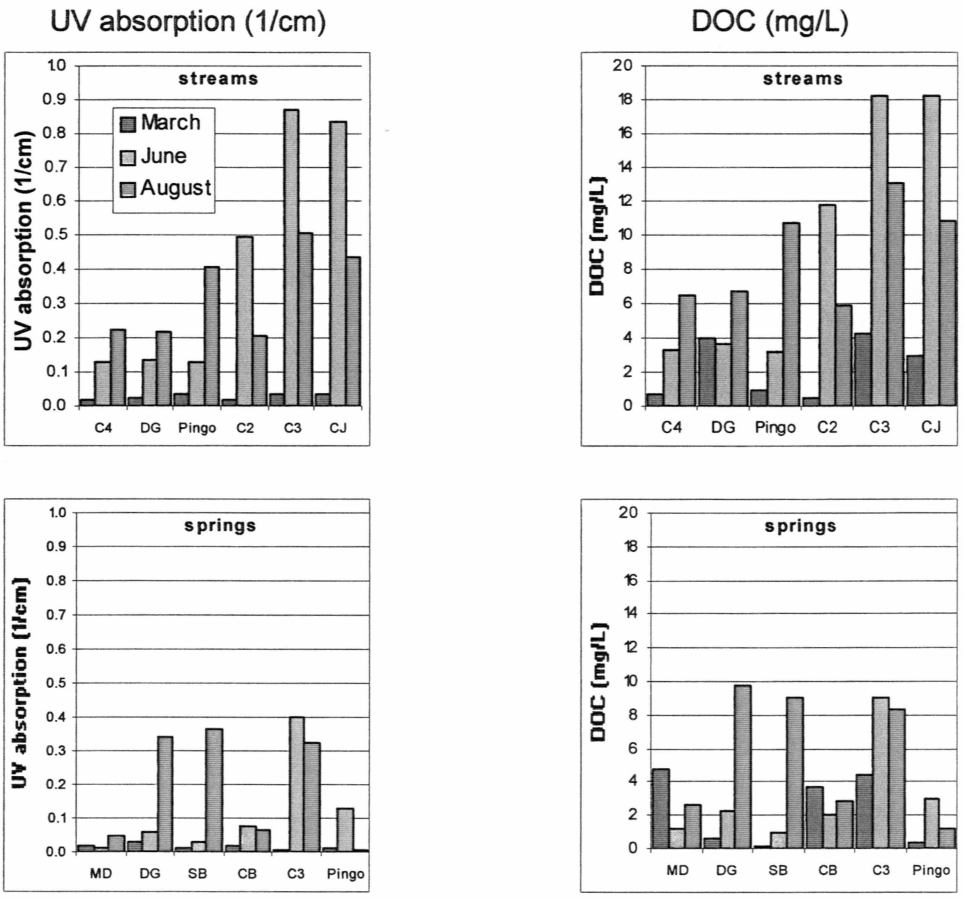


Figure 2.4 Evolution of the UV absorbance, and DOC for each sampling sites

UV-254 Absorption versus Dissolved Organic Carbon, A/DOC

For aquatic systems, NOM can be differentiated according to its origin as pedogenic or aquagenic. Pedogenic NOM (POM) is soil derived and largely results from the decomposition of higher plants by bacteria and fungi. Aquagenic NOM (AOM) is derived from aquatic plankton and bacteria. In general, AOM can be distinguished from soil by the absence of lignin. The UV-absorption measures the concentration of aromatic structures in NOM. Since aromatic structures are abundant in lignin, POM generally has a higher UV-absorbance. UV-absorbance in the vicinity of 280 nm, is particularly

effective at distinguishing POM since 280 nm corresponds to the range of maximum absorption for most phenolic and benzene carboxylic compounds (Buffle J. 1990). In this study a UV-absorbance at 254 nm was used. UV-absorbance at 254 nm is also representative of an aromatic signal and is a more common standard for water quality.

Based on Figure 2.5, the relationship between UV absorption and DOC shows that stream samples taken in June and August contain a much stronger tendency towards POM. The same is true for springs. March samples lacked a strong POM signal.

Both spring and stream present a similar correlation between absorption and DOC, however, the spring data were more scattered and showed diversity. This was expected since the DOC, in general, was consistent among streams and quite variable for springs. The lack of a strong POM signal in the March samples cannot be interpreted to mean that the samples were primarily derived from aquatic materials. Rather it is more likely that the POM signal was depleted through biological degradation in the subsurface (Beaulieu, 2000). The relationship between UV absorbance and DOC for the springs appeared to be strongly influenced by seasonal infiltration. If the springs were fed by groundwater only, the seasonal signature would not differ from the March samples. The fact that the slope of the A/DOC relationship was weaker in spring than in stream samples is likely the result of the different infiltration mix ratios in each individual spring.

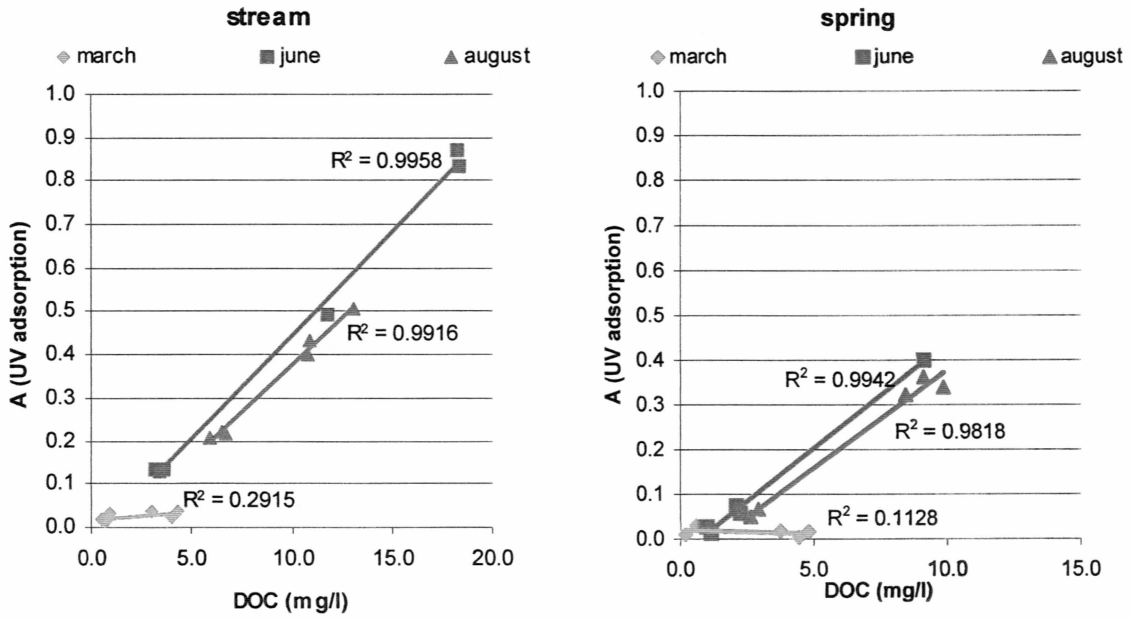


Figure 2.5 Absorption/Dissolved Organic Carbon of stream and spring.

Pyrolysis

The nature and concentration of organic compounds in water results from an extremely complex set of processes among which are production and degradation of terrestrial and aquatic biomass, leaching of soil by rainfall, adsorption reactions on suspended particles, particle coagulation and sedimentation in water bodies, chemical and biological activity in sediments, and entrainment of aerosols (J. Buffle 1990). Therefore, the composition of organic substances can vary dramatically from one water system to another, even in the same system. Unfortunately, the bulk quantification techniques, such as DOC, provide no information about the composition of organic matter (e.g., sugars, proteins, lignin). Therefore the method used by White and Beyer

(1999), was used herein to learn more about the composition of DOC in the streams and springs.

In order to distinguish between different types of organic matter, the relative abundance of a suite of compounds in each sample were compared. The relative abundance allows a direct comparison of changes to the organic matter composition, but does not indicate a change in mass. For example, the decrease in relative abundance of a specific compound does not mean that the absolute abundance decreased, only that the abundance of other compounds increased in greater proportions. The organic matter was divided into methyl benzenes, benzonitriles, furfurals and methylcyclopentanone. While methylbenzenes are not specifically derived from lignin, aromatic compounds, such as methylbenzene are indicative of ligninaceous input. Benzonitriles are also aromatic compounds but can be linked more to protein production than lignin. Furfurals are a signal of primary and secondary sugars in the soil. Cyclopentenones are known to be derived from a variety of sources, primarily carboxylic acid moeties.

C3 and Pingo streams for which the methylbenzene was high in March (> 15% of index) had a low increase of methylbenzene in June and August. Benzonitrile level, being already low in March, continued to slowly decrease in June and August. C3 stream is correlated to Pingo stream by a factor of 0.99.

In contrast to other streams, C2, C4 and DG stream, which had a low level of methylbenzene (< 15% of index) in March, increased the level of the same compound by approximately four, in the following months. Yet, the high level of benzonitrile (≈ 50% of index) in March decreased substantially in June and August. C4 is correlated to C2 and DG stream by 0.89 and 0.97 respectively.

C2, C3, and Pingo streams are situated in Caribou creek watershed, and C4 and DG streams are situated in Little Poker Creek watershed. The seasonal variation of the organic matter chemistry of those two watersheds was different. However, C2 stream was better correlated to C4 and DG streams, with correlation factors being 0.89 and 0.90, respectively, than to C3 and Pingo streams. Approximately 27% of the Caribou Creek watershed is underlain by permafrost whereas only 18% of the Little Poker Creek watershed is underlain by permafrost. Since, C2 sub-watershed had only 3.5 % of its total area underlain by permafrost, it was expected that the organic matter chemistry of C2 streams be better correlated to Little Poker Creek streams.

CJ stream being the outlet of the watersheds, was therefore receiving the different characteristics of each streams, thus CJ stream characteristic was an average of the previous streams.

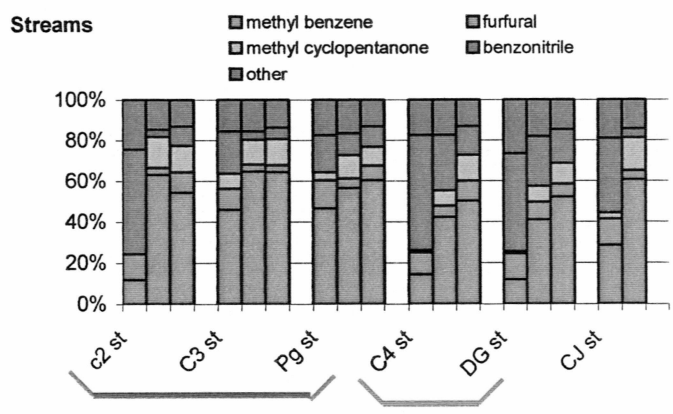
As a whole, nitriles decreased and alkyl benzenes increased. This was expected since nitriles are believed to be derived from protein accumulating from microbial degradation of organics in the subsurface, and, alkyl benzenes are believed to be derived from decomposing lignin rich plant material, most available for transport over the summer.

C3 and CB springs had a level of methylbenzene averaging 50% during March-August period, which increased during that same period. Their lower level of benzonitrile decreased from March to August. C3 spring is correlated to CB spring by a correlation factor of 0.93.

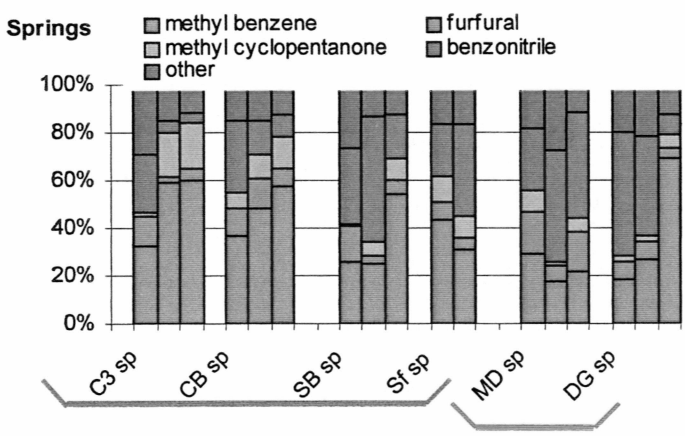
On the difference to SB, SF, MD and DG springs, which had a lower level of benzonitrile averaging 35% during March-August period. The level of methylbenzene

stayed constant throughout the period, or increased in August for SB and DG springs. However, the average methylbenzene level of SB, SF, MD and DG spring stayed lower than for C3, CB, and Pingo springs. SB is correlated to SF, MD and DG spring, by 0.76, 0.62 and 0.90, respectively.

Caribou Creek springs were not found to be distinctively different than Little Poker Creek springs, in the exception of C3 and CB springs. This was expected since the spring water remained in the ground for several years, and its original signal identity (possibly strongly diversified) was lost or diminished due to physical, chemical and biological changes. C3 and CB springs might support shallower water, or water had a shorter residence time. However, organic matter chemistry of stream and spring changed over time.



	C3 st	Pg st	C4 st	DG st	CJ st
c2 st	0.79	0.75	0.89	0.90	0.93
C3 st		0.99	0.65	0.67	0.91
Pg st			0.64	0.67	0.86
C4 st				0.97	0.72
DG st					0.74



	CB sp	SB sp	Sf sp	MD sp	DG sp
C3 sp	0.93	0.54	0.46	-0.05	0.61
CB sp		0.64	0.65	0.12	0.75
SB sp			0.76	0.62	0.9
Sf sp				0.75	0.58
MD sp					0.41

Figure 2.6 Index (Table 2.1) evolution for streams and springs, during the period March-August. Correlation between streams or springs compounds during the same period.

The dimethylbenzene compound reflects the DOC evolution. The DOC-dimethylbenzene correlation is of significant importance. For example, MD, DG and C3 springs are correlated by 1.00, 1.00 and 0.99 respectively. C2, C3 and C4 streams are correlated by 0.92, 0.94 and 0.94, respectively. Thus, dimethylbenzene compounds might be the reason in a DOC change during the course of a year.

Table 2.2 DOC-Dimethylbenzene correlation for each spring and stream.

C4 stream	0.94
DG stream	0.63
Pingo stream	0.85
C2 stream	0.92
C3 stream	0.94
MD spring	1.00
DG spring	1.00
SB spring	0.99
CB spring	-0.58
C3 spring	0.99

CONCLUSION

The seasonal variation in true color, ultraviolet absorbance at 254 nanometers (UV_{254}), and DOC concentration for 6 different streams and 6 different springs were compared. The seasonal variation of the true color, UV_{254} and DOC showed two distinct groups. One with higher values occurring in the late summer, and the other with higher values in early summer. The research also showed that there was little difference between true color-UV_{254}-DOC relationship between spring and stream samples, though streams carried more NOM than springs year round. However there was a significant difference in this relationship as a function of sample collection time (i.e. March, June, August).

Using pyrolysis-GC/MS, a suite of molecules was selected to look at changes in the molecular composition of DOM in CPCRW. There was a significant difference of the molecular composition of the DOM as function of season. The most pronounced difference was an abundance of nitriles and a lack of alkylbenzenes in the March pyrolyzates when compared to June and August samples. These results were expected since the nitriles are believed to be derived from proteins accumulating from microbial degradation of organics over the winter. The alkyl benzenes, believed to be derived from decomposing lignin-rich plant material, were more abundant in the summer when material from the surface runoff enters surface water bodies.

Results from this research suggest that the organic matter abundance and molecular composition change appreciably over the course of the year.

REFERENCES

1- Beaulieu S. (2000). *Importance of benthic-pelagic coupling in the ocean carbon cycle.* Applied Ocean Physics and Engineering Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543. http://www.whoi.edu/science/AOPE/cofdl/stace/OCTET_EDOCC.htm

2- Buffle J., *Complexation reactions in aquatic systems; Distinction between aquagenic and pedogenic NOM,* Ellis Hordwood (1990), 122-132

3- Buffle J. and Deladoey P. 1982 *Schweiz. Z. Hydrol.* 44, 363

4- Collins, C.M., 1986. *The installation of long term ground temperature monitoring sites in the Caribou-Poker Creeks Research Watershed.* Technical note. NH: U.S. Army Cold Region Research and Engineering Laboratory.P.28

5- Clesceri L.S., Greenberg A.E., and Deaton A.D., eds., 1998. *Standard Methods for the Examination of Water and Wastewater, 20th ed.* American Public Health Association, American Water Works Association, Water Environment Federation, Washington, D.C.

6- Fedeler B., 2001 University of Minnesota Duluth, Natural Resources Research Institute http://wow.nrri.umn.edu/wow/teacher/conduct/teaching.html

7- Forbes, R.B., and Weber, R.R., 1982: *Bedrock geologic map of Fairbanks mining district*, Alaska. Alaska Division of Geological and Geophysical Surveys, open file report 170.

8- Lawson, D.E., Arcone, S.A., Collins, C.M., 1991. *Geophysical investigations of an anomalous unfrozen zone, Caribou Peak, Alaska.* CRREL Report Number 91-17. Hanover, NH: U.S. Army Cold Region Research and Engineering Laboratory.P.24

9- Leya T., Müller T., Ling H. U., Fuhr G. (2000) *Taxonomy and biophysical properties of cryophilic microalgae and their environmental factors in northwest Spitsbergen, Svalbard.* 57th Eastern Snow Conference, Syracuse, New York, USA.

10- Stevenson, F.J., 1994: *Soil lipids.* P169. Humus chemistry, Genesis, Composition, Reactions. Jhon Wiley & Sons, Inc

11- White D.M. and Beyer L., 1999. *Pyrolysis-GC/MS and GC/FID of three Antarctic soils*, Journal of Analytical and Applied Pyrolysis, Vol. 50, p63-76

12- White D.M. Yoshikawa K., and Garland S. 2002. *Use of dissolved organic matter to support hydrologic investigations in a permafrost dominated watershed.* Cold Regions Science and Technology. Accepted for publication.

CHAPTER 3. Hydrology of the boreal watershed, Caribou-Poker Creeks Research Watershed[1]

Abstract - Understanding the subsurface hydrology in a discontinuous permafrost environment is of great importance to predicting transport mechanisms of natural organic matter (NOM) and contaminants. In order to gain better insight into NOM transport in the discontinuous permafrost environment, a study was conducted in the Caribou-Poker Creeks Research Watershed (CPCRW).

The central hypothesis for this research was that water could be traced to its origin through a correlation of NOM fingerprints. One hypothesis was that the water appearing on the north-facing slopes (i.e. discharge area) was derived from infiltration at higher elevation on the south-facing slopes (i.e. recharge area). Another hypothesis was that surface water in downstream segments could be correlated with an upstream source, and that this relationship would change during the course of the year.

The chemistry of dissolved organic matter (DOM) of different water sources (i.e. groundwater, artesian spring and stream) was analyzed using pyrolysis-gas chromatography/mass spectrometry (py-GC/MS). The py-GC/MS is an analytical tool used to produce a "fingerprint" of dissolved organic matter (DOM) in water (White et al, 2002). A correlation of the fingerprints was used to characterize relationship between individual samples and between watersheds. In addition, the fingerprints of spring organic matter (OM) were compared between March 2000 data set (White et al, 2002) and March 2001 data set.

---

[1] This chapter is in preparation for submittal as Autier and White, "Hydrology of a boreal watershed, Caribou-Poker creeks research watersheds" to Water Research

The results suggested that spring waters emerging on the north-facing slope (discharge area) could be derived from groundwater at higher elevation on south-facing slopes (recharge area), but that a fault system was further complicating hydrology in the area. Also, the downstream water was found to be well correlated with its upstream or groundwater source in winter. This correlation decreased in summer, probably due to the contribution of surface runoff into the streams. The results also suggested that the OM chemistry of the Little Poker Creek watershed's springs were less subjected to changes than the OM chemistry of the Caribou Creek watershed's springs, between 2000 and 2001.

INTRODUCTION

It is important to understand groundwater hydrology when trying to define where contaminants may be transported in the subsurface. Organic and inorganic tracers are often used to determine groundwater flow paths where groundwater has a very short residence time. Unfortunately, when the water is in the subsurface for periods of years to decades, conservative tracers, such as dyes, are not effective. In such a case, natural tracers with unique characteristics can be used to describe the source or flow path of surface or subsurface water. Organic and inorganic tracers, used in combination, provide the strongest evidence for flow path identification where artificial tracers are not practical. This research extends a previous effort to use organic matter fingerprinting as a method for characterizing groundwater origin and pathway in a permafrost dominated watershed.

South-facing slopes are permafrost free (Lawson et al, 1991) and were therefore considered as recharge area. Haystack groundwater, TR1 spring and SF spring were situated on south-facing slopes and were representing recharge areas. Permafrost dominates valley bottom and/or north-facing slopes (Haugen, 1982; Appendix 1). Therefore, valley bottom and north-facing slopes were considered and represented discharge areas, comprising all other sampled springs of the research (i.e. DG, MD, SB, Pingo, TR6, C3, and CB).

High correlation between the fingerprints of the recharging and discharging areas bear two meanings, either the water are hydrologically connected or have undergone similar processes. It is not possible to define which of the two possibilities is correct by simply looking at the correlation. This is one limitation of the technique used.

MATERIALS AND METHODS

Site Description

Field research was conducted in the Caribou-Poker Creeks Research Watershed (CPCRW), 48 km northeast of Fairbanks Alaska. The CPCRW is an important component of the Bonanza Creek Long Term Ecological Research (LTER) Program. LTER maintains reliable hydrological and meteorological measurements for use of worldwide scientists. The CPCRW lies at latitude 65°10'N, longitude 147°30'W. The area is underlain by discontinuous permafrost. In general, north-facing and shaded slopes and valleys are underlain by permafrost with depth ranging from 10 to 50 m (Haugen, 1982). South-facing slopes and sites of historical forest fires may be entirely free of

permafrost. In areas where permafrost has been degraded, thermokarst is a dominant surface feature. There are several faults that pass through the CPCRW complicating groundwater hydrology. For instance, one fault passes generally east west through the C3 watershed (Forbes and Weber, 1982). In addition, there was in 1924 a forest fire that burned most C3 watershed, and a prescribed burn in the C4 watershed in July 1999 during four days, burning part of the north-facing slope of the watershed. The CPCRW also contains two pingos, an active pingo and a collapsed pingo, adjacent to Caribou Creek.

Springs flow year-round on north and south-facing slopes. The confining layer on north-facing slopes is thought to be the permafrost itself whereas the springs flowing off south-facing slopes emerge from cracks in bedrock. Bedrock in the CPCRW is predominantly fractured and weathered schist (Collins, 1986). The Caribou-Poker Creeks Research Watershed is entirely underlained by the Yukon-tanana metamorphic complex (Ray, 1988). Chapman et al. (1971) described the complex in the watershed as a greeschist facies, dominated by chlorotic and quartz-mica schists, with some micaceous quartzites, garnet-mica schists, phyllites, and possible greenstone or impure marbles. The origin of groundwater emerging from artesian springs on north-facing slopes is thought to be derived from water infiltrating at higher elevation on the south-facing, permafrost free slopes outside the topographic watershed boundaries (Lawson et al, 1991). South-facing area will be considered as recharge area, comparatively to north-facing area being considered as discharge area. The residence time of the artesian spring water was determined to be about one to three decades, by CFCs and tritium analysis (Yoshikawa et al, 2002).

Sampling in the Field

Samples were collected during 2001 in March (winter season: minimal water flow in streams, frozen active layer), and June (spring break up, 9 months of accumulated precipitation is thawing as well as the ground). The dates of sampling events are shown in Figure 3.1. In total, 9 springs, 6 streams, and one well were sampled (Figure 3.2).

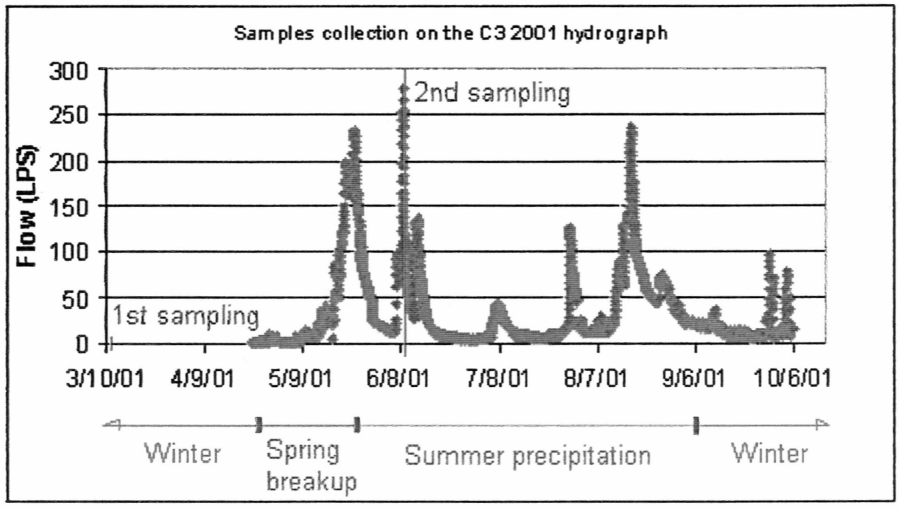


Figure 3.1 sampling collection period superposed on the C3 2001 hydrograph

Spring samples were collected using a 60 ml syringe to draw 4 liters of water from clear flowing water at the origin of the spring. Stream samples were collected as grab samples from below the water surface. Finally the ground water sample was collected from a domestic water well at the tap. For all samples, 4 liters of water were collected, using 1-liter amber glass bottles. The conductivity and temperature of the water samples were determined *in situ*. The bottles were then set in a cooler and brought back to the UAF laboratories where additional tests were performed. The glass bottles were stored in a refrigerator at 4°C.

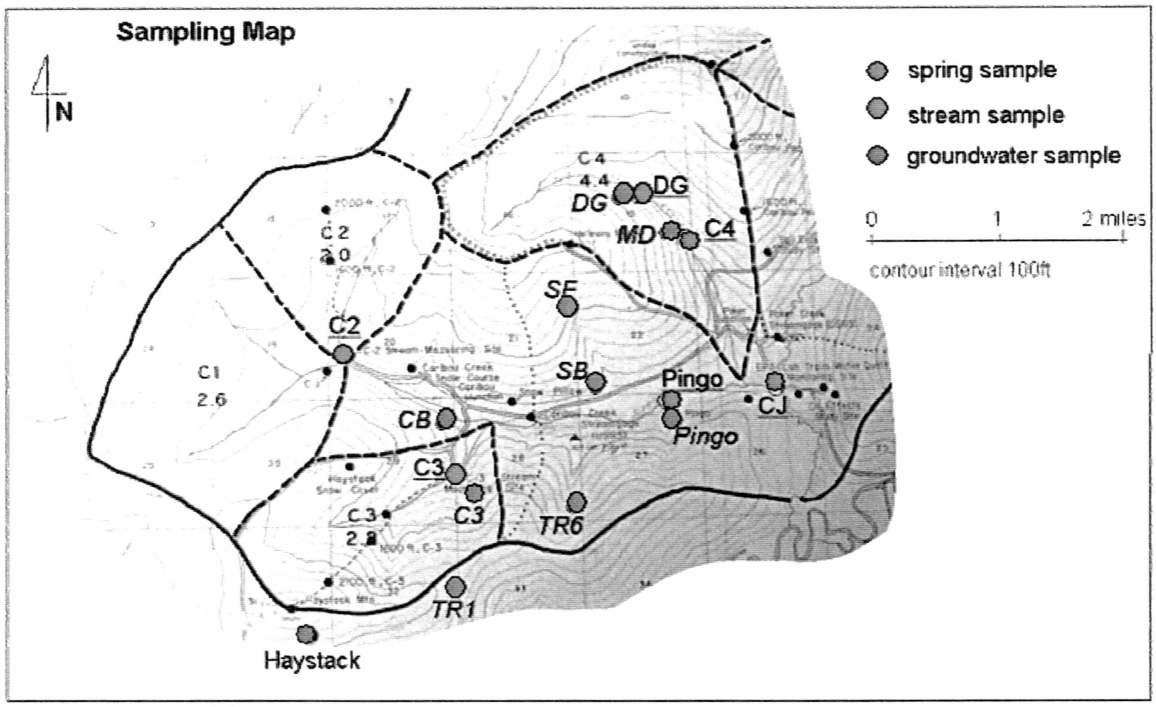


Figure 3.2 Sampling map of different water sources in the CPCRW.

Water Analysis

Sample Preparation

Samples were filtered at 0.3 μm on a glass fiber filter and refrigerated at 4°C until analyzed. Two liters of each sample were dried in a Büchi RE-111 Rotovap vacuum evaporator at 40°C to a volume of approximately 20mL. This concentrate was poured into a 4oz jar and placed in a drying oven at 60°C to finalize the drying. When dry, the residue was scraped free from the jar, ground to a fine powder with a stainless steel spatula, homogenized and stored in a dessicator until analyzed by pyrolysis-GC/MS. A portion of the powder, equal to the yield from approximately 0.5mg of DOC, was placed in a quartz sample tube for pyrolysis. (Each sample tube was injected with an internal standard consisting of 0.4μg of poly-α-methyl styrene in 4 μl of methylene chloride).

Pyrolysis-GC/MS Analysis

Py-GC/MS was conducted with a CDS Pyroprobe 2000 pyrolyzer with AS2500 auto sampler, mounted on an HP 6890 Gas Chromatograph with a Restek Rtx35-MS column, 30 m x 0.32 mm x 0.25 µm. Pulsed split less injection was used, with pulse pressure 25 psi. The pyrolysis interface and GC injection port were kept at 280°C. Before pyrolysis, the sample was held in the 280°C chamber for 15 seconds while the chamber was purged with helium carrier gas. The pyrolyzer was then switched online to the GC and pyrolysis began. The pyrolyzer temperature was ramped at 10°C/ms to 700°C and held constant for 10 seconds. After one minute, the pyrolyzer was switched offline and column head pressure was reduced to provide constant flow of helium at 2.0 ml/min. The GC temperature program was 40°C for 30 minutes, then ramp at 1°C /min to 120°C. A final ramp at 10°C /min to 280°C and hold for 10 min was used to clean out the column in preparation for the next sample. The GC was plumbed directly to an HP 5973 Mass Selective Detector on electron impact (EI) mode. The MS scanned mass units 45 to 350. All mass spectra were compared to the Wiley 275 spectral library.

Following the pyrolysis of DOM, a complex chromatograph was generated. The chromatograph represents the abundance of each compound of the NOM versus time (Figure 3.3). For this study, an index of 11 compounds was selected (Table 3.1). This index represents the chromatograph. It is important to note that those compounds were the results of pyrolysis and are not necessarily found as such in the water. HP Chemstation software was used to extract and integrate ion chromatograms of the most abundant ion of each compounds of the index.

Once a single "fingerprint" was generated for each sample, the fingerprints could be correlated. A fingerprint is the relative abundance of each compound of the index to the sum of the relative abundance of all compounds of the index (Table 3.1). The relative abundance was expressed in percent. The correlation was based on the differences and/or similarities between fingerprints of each sample.

For this research, "high" correlation factor was set as being equal to or greater than 0.8. High correlation will be accepted, and low correlation will be rejected. High correlation between two water sample fingerprints (i.e. relative chemical composition) could signify that one of/or two following water behavior hypothesis would be accepted. The first hypothesis is that if the correlation is high, the chemical composition of those two water sources is similar, and the waters are hydrologically connected. The second hypothesis is that the waters have undergone similar processes but are not hydrologically connected.

Table 3.1 Selected pyrolysis products or index (PCA = polycarboxylic acids, PAH = poly-aromatic hydrocarbon, P = polysaccharides, L = lipids, Pr = proteins).

#	*Compound*	*Possible origin*
1	dimethyl benzene	PAH
2	furfural	P
3	methyl cyclopentenone	PCA
4	trimethyl benzene	PAH
5	benzaldehyde	
6	benzofuran	P
7	benzonitrile	Pr
8	phenyl ethanone	
9	methyl benzonitrile	Pr
10	Azulene	L
11	2-methyl Naphtalene	L

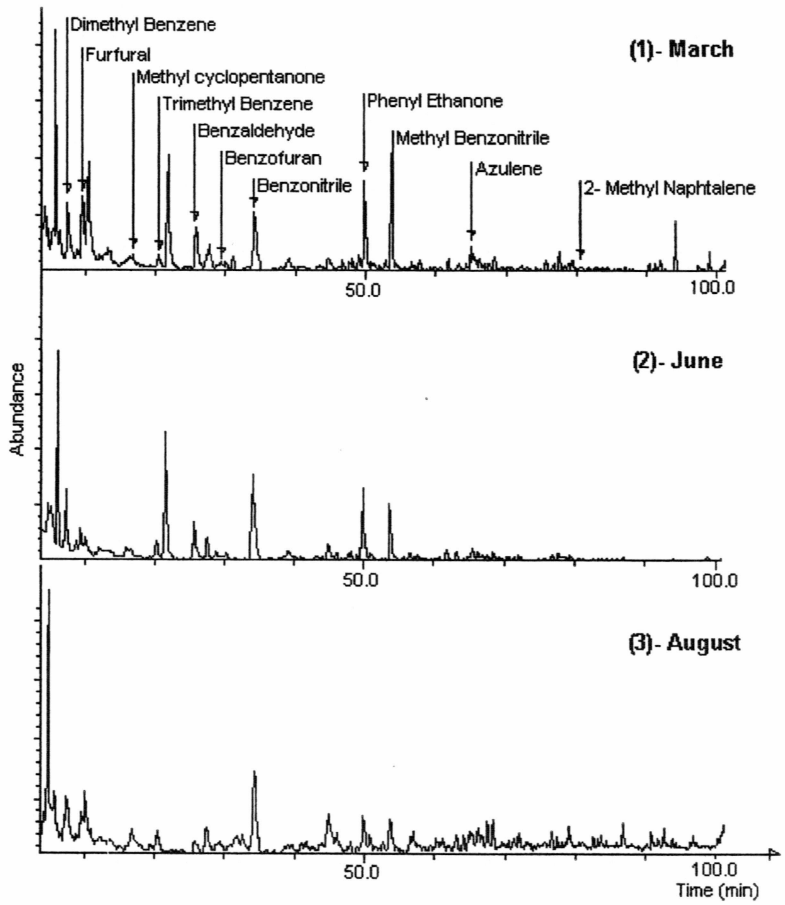


Figure 3.3 Chromatograph, representing the change in chemical composition of a sample, between March (1), June (2) and August (3). The index is reported on Table 3.1.

RESULTS

In all cases, the correlation was based on the identity (i.e. fingerprint) of the water samples. The relative abundance of each compound was found by comparing it to the sum of the relative abundances of the eleven compounds of the index (Table 3.1). The relative abundance was expressed in percent. For example, in Figure 3.4, each point represents the relative abundance of each molecules in the pyrolyzates of stream

samples C2 and C3 in June showing high correlation. The correlations for each of these samples are (r) and are listed in tables 3.2 and 3.3, depending on the sampling period.

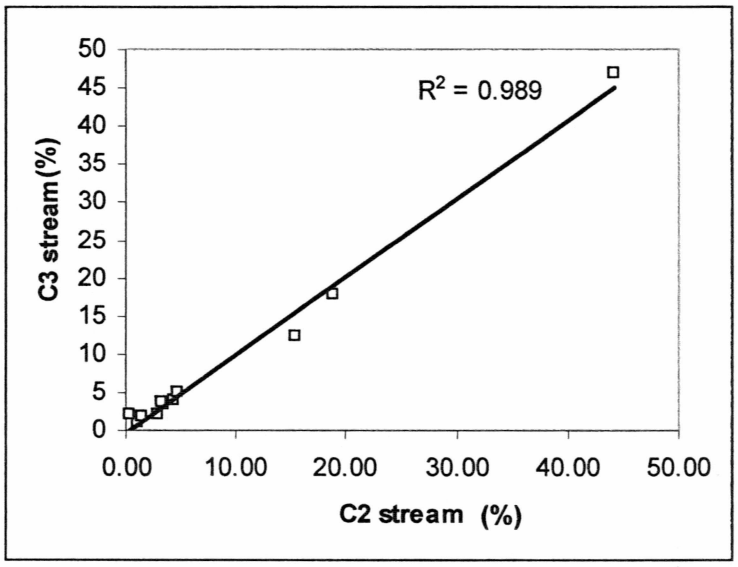


Figure 3.4 Comparison of the relative abundance of index compounds for spring C2 and C3.

Table 3.2. Correlation coefficients, based on the sum of the individual relative abundance of each compounds, between water samples for March 2000 sampling event (white et al, 2002)

Mar-00	C3 stream	C4 stream	CJ stream	Dry Gulchstream	Pingo stream	Haystack	C3 spring	CB spring	Dry Gulch spring	MD spring	Pingo spring	SB spring	Sf spring	TR1 spring	TR6
C2															
C3 stream															
C4 stream															
CJ stream															
Dry Gulchstream						0.47	0.75	0.73	0.89	0.93	0.07	0.37	0.96		
Pingo stream															
Haystack							0.93	0.87	0.80	0.51	-0.03	0.50	0.55		
C3 spring								0.95	0.96	0.78	0.06	0.56	0.80		
CB spring									0.96	0.83	0.29	0.65	0.83		
Dry Gulch spring										0.90	0.16	0.56	0.93		
MD spring											0.34	0.50	0.93		
Pingo spring												0.48	0.23		
SB spring													0.45		

Table 3.3. Correlation coefficients, based on the sum of the individual relative abundance of each compounds, between water samples for March 2001 sampling event

MARCH	C3 stream	C4 stream	CJ stream	Dry Gulchstream	Pingo stream	Haystack	C3 spring	CB spring	Dry Gulch spring	MD spring	Pingo spring	SB spring	Sf spring	TR1 spring	TR6
C2	0.36	0.99	0.89	0.99	0.34	0.99	0.64	0.74	0.98	0.69	0.03	0.88			
C3 stream		0.40	0.71	0.37	0.87	0.38	0.79	0.88	0.47	0.82	0.91	0.60			
C4 stream			0.91	0.99	0.37	1.00	0.66	0.78	0.99	0.71	0.08	0.87			
CJ stream				0.89	0.68	0.88	0.83	0.95	0.94	0.85	0.44	0.87			
Dry Gulchstream					0.33	0.98	0.63	0.74	0.97	0.70	0.05	0.86			
Pingo stream						0.33	0.69	0.81	0.43	0.67	0.75	0.56			
Haystack							0.63	0.75	0.98	0.66	0.03	0.84			
C3 spring								0.86	0.68	0.80	0.69	0.75			
CB spring									0.81	0.92	0.64	0.84			
Dry Gulch spring										0.70	0.14	0.83			
MD spring											0.63	0.84			
Pingo spring												0.34			
SB spring															
Sf spring															
TR1 spring															

Table 3.4 Correlation coefficients, based on the sum of the individual relative abundance of each compounds, between water samples for June 2001 sampling event

June	C3 stream	C4 stream	CJ stream	Dry Gulchstream	Pingo stream	Haystack	C3 spring	CB spring	Dry Gulch spring	MD spring	Pingo spring	SB spring	Sf spring	TR1 spring	TR6
C2	0.99	0.66	1.00	0.69	0.97	0.16	0.99	0.88	0.12	-0.07	0.92	0.05	0.31		-0.03
C3 stream		0.71	0.99	0.73	0.98	0.21	0.98	0.89	0.18	-0.01	0.91	0.10	0.35		0.01
C4 stream			0.68	0.99	0.81	0.84	0.68	0.87	0.82	0.67	0.63	0.77	0.91		0.31
CJ stream				0.71	0.97	0.18	1.00	0.89	0.14	-0.04	0.93	0.08	0.33		-0.01
Dry Gulchstream					0.83	0.79	0.70	0.90	0.78	0.65	0.70	0.73	0.88		0.66
Pingo stream						0.38	0.97	0.95	0.34	0.15	0.90	0.27	0.50		0.18
Haystack							0.20	0.51	0.97	0.92	0.16	0.99	0.98		0.97
C3 spring								0.88	0.14	-0.03	0.93	0.09	0.35		0.01
CB spring									0.49	0.30	0.92	0.41	0.62		0.31
Dry Gulch spring										0.92	0.15	0.98	0.95		0.95
MD spring											-0.02	0.94	0.89		0.94
SB spring													0.96		0.99
Sf spring															0.93
TR1 spring															0.09

DISCUSSION

The central hypothesis for this research was that water emerging from springs on north-facing slopes, rich in permafrost, originated from higher elevations on the south-facing slopes. This hypothesis has been described previously (White et al 2002, Yoshikawa et al, 2002). The springs transect, shown in Figures 3.5 and 3.6, illustrate this hypothesis. Based on this hypothesis, the DOM fingerprint of samples collected on recharge area (higher elevations on the south-facing slopes) should be well correlated to discharge area (opposing north-facing springs).

Origin of the water on the North-facing slopes for March sampling

In a previous study conducted in 2000, White et al. 2002, found the Haystack groundwater to be well correlated to the two respective south-facing springs, C3 spring and CB spring by coefficients of 0.93 and 0.87, respectively. By March 2001, these correlations had dropped to 0.63 and 0.75, respectively. Although these values suggest some correlation, this change was considered significant since only one year had passed since the 2001 sampling event. The most significant change was between Haystack and C3 spring. A correlation coefficient of 0.63 suggests that the two waters were not derived from a similar source, as they seemed to be in 2000. In 2000, the conductivity for Haystack, C3 spring and CB spring was 120, 113, and 118 µS/cm, respectively. In 2001, these values had changed to 120, 198, and 121 µS/cm. Thus, Haystack groundwater and CB spring remained constant, in the opposite of C3 spring, which changed from 2000 to 2001.

A change of spring water conductivity can be natural (i.e. small change) or due to surface water contamination (i.e. in general a substantial change). The large difference of conductivity between 2000 and 2001 for C3 spring implies that C3 spring was contaminated in March 2000. A higher conductivity signifies more dissolved salt and most likely, more subsurface residence time. Surface flow or intra flow are normally low in dissolved, thus having low conductivity. Therefore, when C3 spring emerged to the surface in 2000, it would have been contaminated with intra flow or surface water (probably higher air temperature in 2000 than in 2001). Thus a comparison of C3 spring conductivity between 2000 and 2001 was not representative.

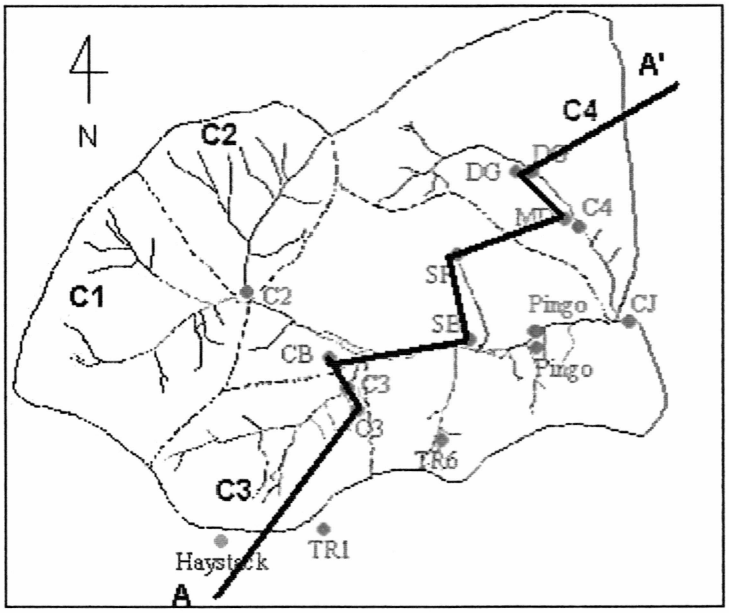


Figure 3.5 Plan view of the CPCRW; Transect A-A' is shown in Figure 3.6.

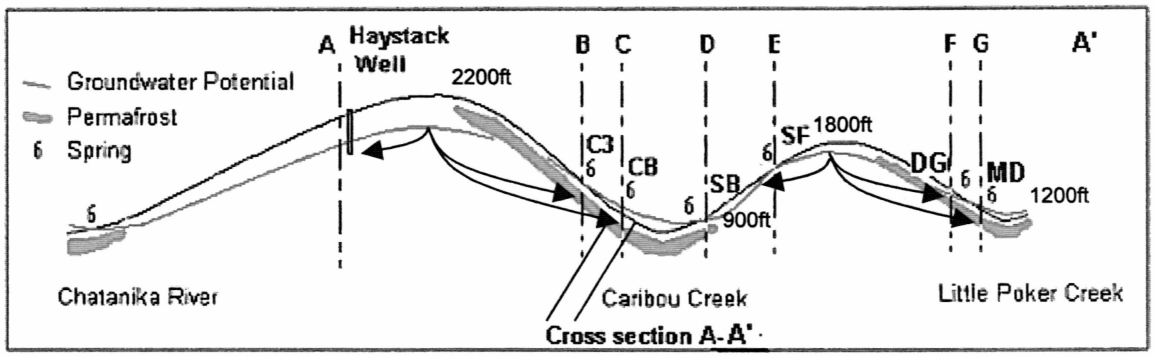


Figure 3.6 Cross section of the CPCRW, representing the springs and the ground water potential.

Samples collected from the SF spring were considered contaminated and not included further in this analysis. In 2000, however, White et al (2002) found that the SF spring was well correlated to MD and DG springs. They also found that Haystack and SF spring had very low correlation to each other.

Although Haystack could have no hydraulic connection to north-facing springs in C4, DG and MD, some correlation was found in the 2000 sampling. The explanation provided by White et al (2002) was that despite having source waters that were not well correlated, the waters emerging from the north-facing springs had undergone enough chemical, physical and biological changes to exhibit some correlation to other water sources, albeit somewhat lower. In White et al (2002) Haystack was correlated to the C4 springs, DG and MD by coefficients of 0.8. In 2001 the correlations were 0.98 and 0.66, respectively. The correlation between Haystack and DG was considerably stronger than observed between Haystack and either of the Caribou Creek watershed springs to which correlation was expected. Another main difference between 2000 and 2001 was the change in the correlation of Haystack to DG spring (higher in 2001). The correlation was 0.80 in 2000, and 0.98 in 2001. This was probably due to a contamination of DG spring in 2001 (see previous discussion about the contamination of C3 spring).

In 2000, the conductivity of samples for Haystack, DG and MD were 120, 75, and 97 respectively. In 2001, the conductivity of the same samples was 120, 87, and 104. The difference in conductivity did not show a dramatic increase in similarity between Haystack and DG or a decrease in similarity between Haystack and MD spring.

The correlation between C3 spring and SB spring was 0.56 in 2000 and 0.84 in 2001, suggesting more connectivity existed between C3 and SB in 2001 compared to 2000. The conductivity of both C3 and SB increased from 2000 to 2001. The conductivity of SB was 155 uS/cm in 2000 and 161 μS/cm in 2001. However, such an increase in correlation was probably not due only to a change in conductivity. The organic matter chemistry also changed (Figure 3.7).

Unlike C3 spring, for which its correlation to Haystack decreased between 2000 and 2001, the correlation between Haystack and SB increased from 0.5 in 2000 to 0.84 in 2001. If C3 spring and SB spring increased in conductivity between 2000 and 2001 one would expect to see an increase in correlation between C3 and SB, an increase in SB and Haystack and a decrease in the correlation between C3 and Haystack. All evidences were observed.

Origin of the water on the north-facing slopes for June sampling

In March 2000, Haystack was correlated to C3 and CB springs by 0.93 and 0.87, respectively. In March 2001, Haystack was correlated to C3 and CB springs by 0.63 and 0.75, respectively. In June, however, Haystack was correlated to C3 spring and CB spring by 0.20 and 0.51 respectively. The correlation between those springs (i.e. Haystack, C3 and CB spring) has been decreasing dramatically. On the other hand, Haystack was correlated to SB spring by 0.50, in March 2000. Haystack was correlated

to TR6 spring and SB spring by 0.97 and 0.99 respectively, in June 2001. An increase of correlation was observed.

In June 2001, SF spring was correlated to DG spring and MD spring by 0.95 and 0.89 respectively. This was expected since the distance between SF spring and DG and MD springs was approximately the same.

The two south-facing groundwater sources at high elevation, SF spring and Haystack were correlated to each other by r = 0.98, both being a recharge area. Water seemed to have undergone similar chemical and/or physical processes. This was much different than the previous years observation in which the two samples were uncorrelated (r=0.45). Likewise the south-facing groundwater should be well correlated to the north-facing springs of the opposite watersheds. Haystack was correlated to DG spring and MD spring, 0.97 and 0.92, respectively and SF spring was correlated to SB spring and to TR6 by 0.96 and 0.93, respectively. The correlation between SF spring and C3 and CB spring should be low. As expected, SF spring is correlated to C3 spring and CB spring by 0.35 and 0.62, respectively.

Furthermore, faults are complicating the system (Forbes and Weber, 1982), (Appendix 3). If a fault system was supporting the high correlation between Haystack and TR6 spring, another fault parallel to the previous one cited would explain the high correlation (r = 0.85) between TR1 and Pingo spring. It was expected to have very low correlation between Haystack and TR1 spring as well as for Pingo spring and TR6 spring, due to the fact that the water would be traveling in two distinct faults, and the TR1-Pingo spring fault would be transmitting older water. As expected the correlations between Haystack - TR1 spring and Pingo - TR6 springs are respectively, 0.28 and -0.02.

Origin of the water in streams; March 2001

The correlation between DG stream and C4 stream was 0.99 and the correlation between C4 stream and CJ stream (outlet of CPCRW watersheds), was 0.99. Therefore the downstream water of the Little Poker Creek was well correlated with its upstream water. The average correlation between the north-facing springs and the stream was 0.84.

Caribou Creek was correlated to its up gradient streams (C2 stream, C3 stream, Pingo stream) by a correlation factor of 0.64. This correlation factor was quite low. Thus, a possible input of water from a different source was decreasing the correlation factor. The two possible sources of water on the south-facing slope could be Haystack ground water or TR1 spring. Haystack was correlated to Caribou Creek stream by a correlation factor equal to 0.65. Also the water emerging in the SB spring is believed to be derived from Haystack ground water ($r = 0.85$), which is itself correlated to the Caribou Creek by a correlation factor of 0.73. TR1 spring was not collected, however Pingo spring is believed to be derived from TR1 and was correlated to the Caribou Creek by a correlation factor of 0.53. This low correlation factor suggests that different water was emerging in the Caribou Creek stream in the area of the collapsed Pingo. Which would be the reason for the low correlation ($r = 0.64$) with the up-gradient streams of Caribou Creek.

Origin of the water in streams; June 2001

Considering Little Poker Creek, the correlation from DG stream to C4 stream was 0.99 and the correlation between C4 stream and CJ stream was 0.68. The fact that the

correlation was greater upstream and decreased downstream indicate that a different water source was contributing to Little Poker Creek. It was expected that this input of water is actually Caribou Creek and not SF spring which is normally thought to be the source of water in the north-facing springs of C4 watershed (i.e. DG spring and MD spring). The correlation coefficient between SF spring and the Little Poker Creek stream was 0.92. Therefore, it was deduced that Caribou Creek, which is connected to Little Poker Creek, was decreasing the correlation between C4 stream and CJ stream. This result was expected since the waters in Caribou Creek and Little Poker Creek seemed to carry a unique fingerprint.

Caribou Creek was correlated to its up gradient streams (C2 stream, C3 stream, Pingo stream) by a correlation factor of 0.98. This high correlation is believed to be derived from high percentage of NOM entering surface water bodies due to surface runoff during spring breakup. Therefore the springs were expected to have a very low correlation factor with the stream. Indeed, Haystack was correlated to the Caribou Creek stream by a correlation factor equal to 0.23. The water emerging in SB spring and TR6 spring was believed to be derived from Haystack ground water with correlation factors equal to 0.99 and 0.97 respectively. In addition, SB and TR6 springs were correlated to Caribou Creek by correlation factors equal to 0.13 and 0.15, respectively.

Evolution of organic matter chemistry between March 2000 and March 2001 for springs

Samples were collected in March 2000 and March 2001. The organic matter chemistry of the Little Poker Creek watershed's springs (i.e. DG sp and MD sp) changed less that the organic matter chemistry of the Caribou Creek watershed's springs (i.e. C3 sp, CB sp, SB sp, and Sf sp). The correlation of the organic matter chemistry, between

March 2000 and March 2001 for Caribou Creek watershed's springs, were equal to 0.40, 0.63, 0.60, and 0.36, respectively. And the correlation of the organic matter chemistry, of the Little Poker Creek watershed's springs, were 0.89 and 0.73 (Figure 3.7). The increase or decrease of the relative percentage abundance of the compounds of the index did not seemed to follow a complex evolution.

The chemical composition of the DOM changed more or less for each spring. The chemical composition changes of the DOM between the year 2000 and 2001 might be due to the infiltration period (1-5 years before present) and/or mixing of the infiltrated water with the resident water. The deviation in composition of the water between the two different periods was not believed to be derived from spring (base flow) contamination by surface runoff (i.e. mixing). Surface runoff, or intraflow in the active layer would clearly influence the chemical composition of the base flow water (springs). The samples were collected in March 2000 and March 2001, when the active layer is believed to be the thickest (Yoshikawa et al., 2002), and therefore when the conditions are the most stable. The deviation in composition was believed to be natural and not being an artifact of the sampling method.

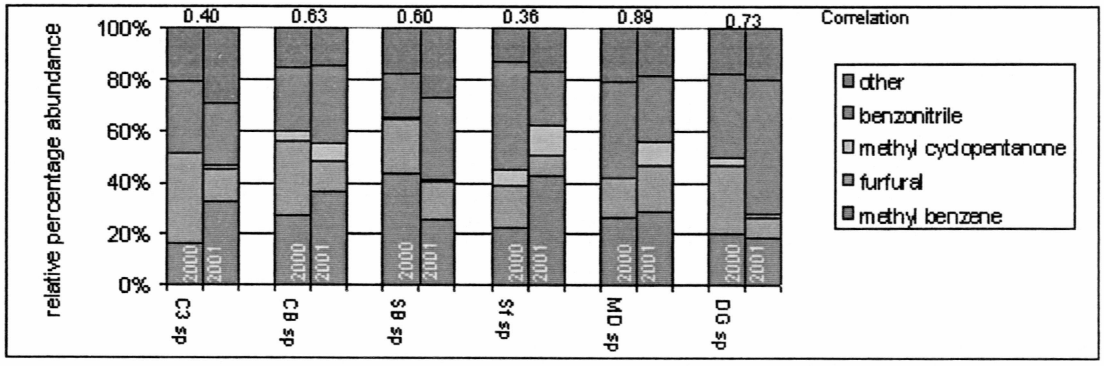


Figure 3.7 Evolution of water chemistry using py-GC/MS, between March 2000 and March 2001

CONCLUSION

The hypothesis was that the water appearing on the discharge area (north-facing slopes) is derived from infiltration on the recharge areas (higher elevations on the south-facing slopes). This hypothesis has been confirmed. However the correlation was slightly less than expected, probably due to contamination of the water samples due to aufeis, lag in collection time, surface water, or/and intra flow.

It was also expected to find the water downstream to be well correlated with an up stream or groundwater source in winter, and the water downstream to be less or not correlated to groundwater source during the summer, due to an increasing amount of NOM in the stream. This was once again verified, for example, SB spring was correlated to Caribou Creek stream by a correlation coefficient equal to 0.73 in March and 0.13 in June.

In addition, the results suggested that the organic matter chemistry of the Little Poker Creek watershed's springs changed less than the organic matter chemistry of the Caribou Creek watershed's springs.

REFERENCES

1- Chapman, R.M., F.R. Weber, and B. Taber. 1971. Preliminary geologic map of Livengood quadrangle. U.S. Geological Survey. Open File Report 483. scale 1:250,000

2- Collins, C.M., 1986: The installation of long term ground temperature-monitoring sites in the Caribou-Poker Creeks Research Watershed. Technical note. NH: U.S. Army Cold Region Research and Engineering Laboratory. P.28

3- Forbes, R.B., and Weber,R.R., 1982 *Bedrock geologic map of Fairbanks mining district, Alaska.* Alaska Division of Geological and Geophysical Surveys, open file report 170.

4- Haugen, R.K.; Slaughter, C.W.; Howe, K.E.; Dingman, S.L. 1982. *Hydrology and climatology of the Caribou-Poker Creeks Research Watershed, Alaska.* CRREL Rep. 82-26. Hanover, NH: U.S. Army Cold Regions Research and Engineering Laboratory. 42 p.

5- Ray, S.R. 1988. Physical and chemical characteristics of headwater streams at Caribou-Poker Creeks Research Watershed, Alaska. Master's thesis, University of Alaska. Fairbanks, Alaska. 172 pp.

6- Rieger, S.; Furbush, C.E.; Schoephorster, D.B.; Summerfield, H., Jr.; Geiger, L.G. 1972. *Soils of the Caribou-Poker Creeks Research Watershed.* Tech. Rep. 236. Hanover, NH: U.S. Army Cold Regions Research and Engineering Laboratory. 11 p

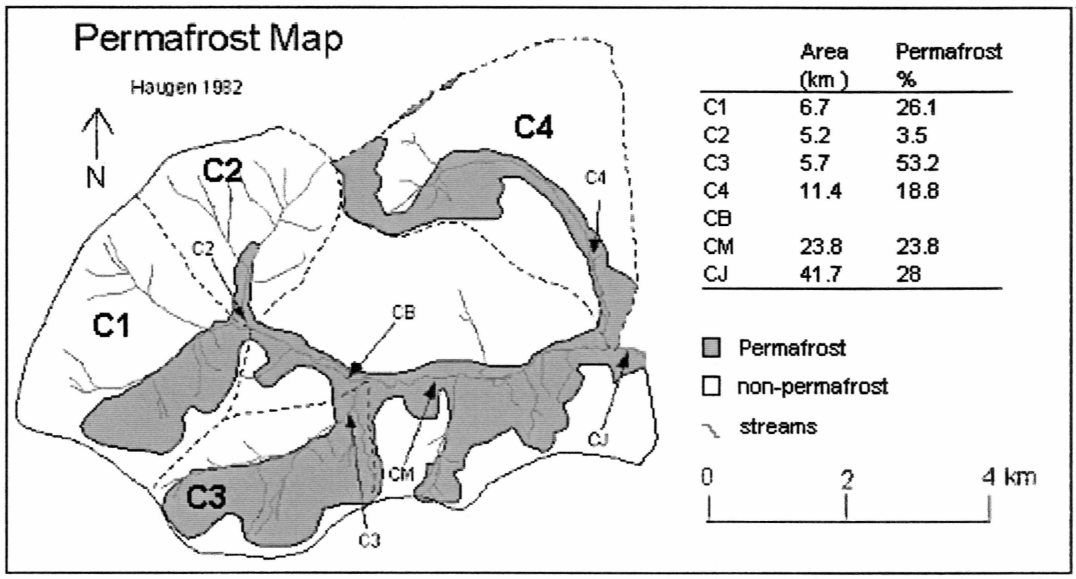
7- Webster, J.R., and J.L. Meyer. 1997. *Stream organic matter budgets.* Journal of the North American Benthological Society 16:3-161

8- White, D.M., Yoshikawa K., and Garland S. 2002. *Use of dissolved organic matter to support hydrologic investigations in a permafrost dominated watershed.* Cold Regions Science and Technology. Accepted for publication.

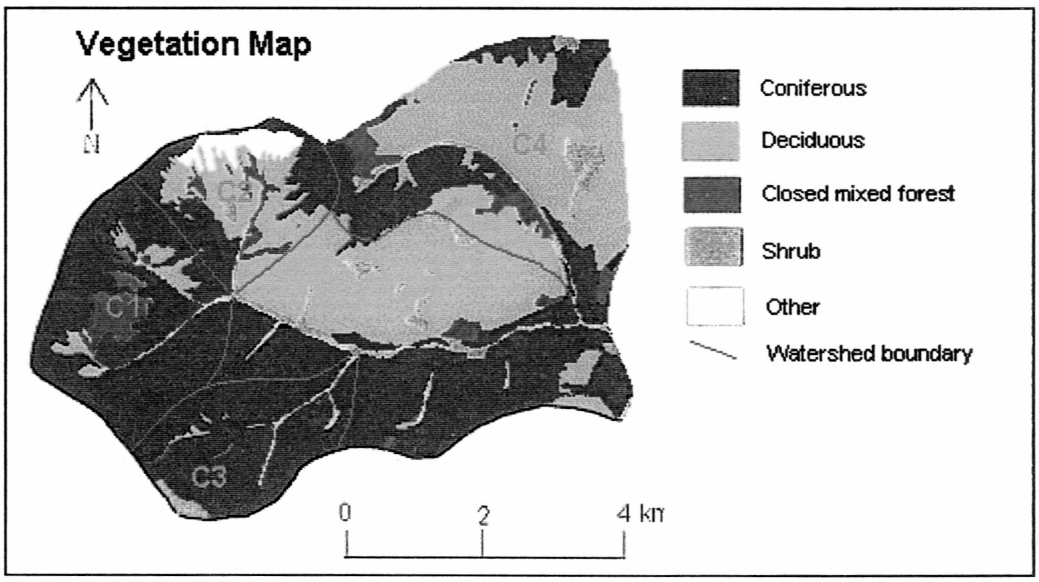
9- Yoshikawa K., D. White, L. Hinzman, D. Goering, K. Petrone, and W. Bolton. Institute of Northern Engineering, University of Alaska Fairbanks, USA (2002); N. Ishikawa, Institute of Low Temperature Science, Hokkaido University, Japan. *Water in*

permafrost; case study of aufeis and pingo hydrology in discontinuous permafrost. Accepted for publication.

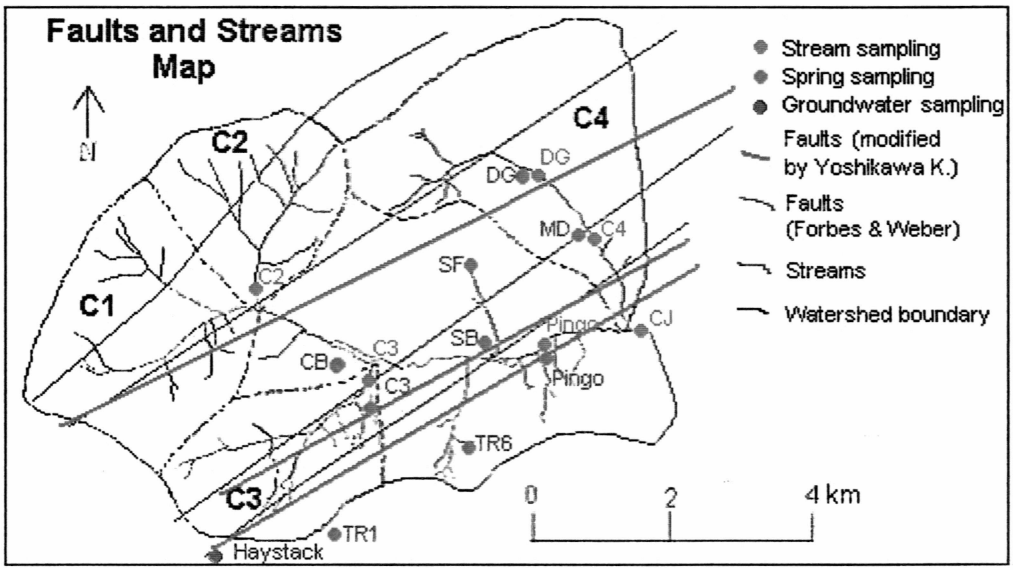
APPENDICES



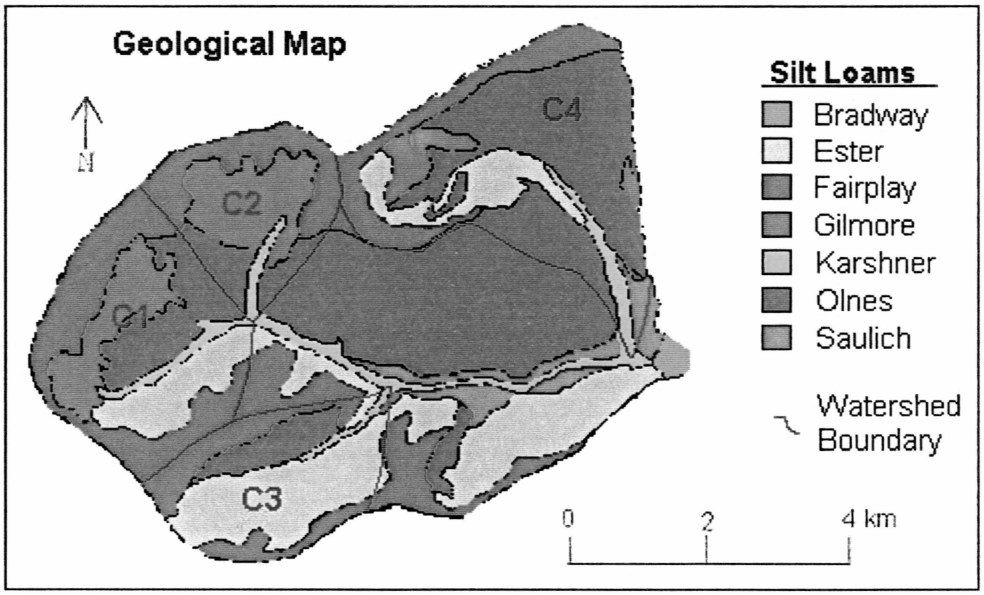
Appendix 1. Permafrost map (Haugen 1982)



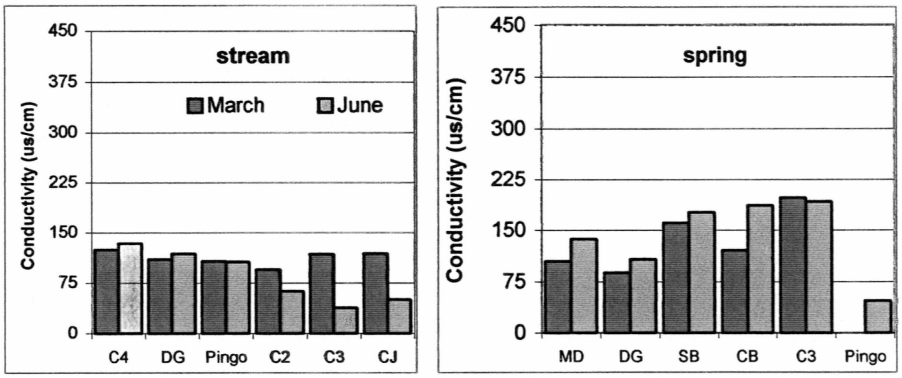
Appendix 2. Modified vegetation map, by Vincent Autier 2002, originally from (Haugen et al 1982)



Appendix 3. Faults map from (Forbes and Weber, 1982).



Appendix 4. Modified Geological map, by Vincent Autier 2002, (Rieger 1972)



Appendix 5. Conductivity evolution of streams and springs for March and June 2001

Appendix 6 Description of soil types found in Caribou-Poker Creeks Research Watershed (Rieger 1972)

Soil Series	USDA Texture	Drainage	Permafrost	Location	% Area
Bradway	Stratified silt loam and loamy sand	poorly drained	shallow	flood plain	1.9
Ester	Silt loam	poorly drained	shallow	steep north-facing slopes	19.1
Fairplay	Silt loam and gravelly silt loam	mod. well drained	none	high ridges above tree line	21.9
Gilmore	Silt loam, gravelly silt loam, and very gravelly silt loam	well drained	none	south-facing slopes	11.5
Karshner	Stratified silt loam, silt loam, very gravelly silt loam, and very gravelly loamy sand	poorly drained	shallow	narrow flood plains in upper channels	1.7
Olnes	Silt loam and very gravelly silt loam	well drained	none	south-facing slopes	39.5
Saulich	Silt loam	poorly drained	shallow	foot slopes of hills	4.4

CONCLUSION AND SUGGESTED FUTURE WORK

The objective of this research was to establish likely sources of Cd mobility in organic rich soils. Results suggested that Cd^{2+} ion was better sorbed by BE horizon, than by AEv or OAe, for the particle size ranging between 0.3 and 75μm. In addition, Cd distribution appeared to be most influenced by the solids distribution. When the amount of material increased the amount of sorbed Cd also increased. However, these results were found on a per mass basis and might differ if the samples would have been further disintegrated (to consider particles and not stable aggregates) and/or if considering the surface area of the particles (Mayer, 1994a).

Cd distribution was well correlated to OM distribution, with correlation factors ranging between 0.95 and 0.94, respectively to particle size. Yet, care should be taken once again. OM are believed to have an affinity for mineral grain surface (Mayer, 1994b). On a surface area basis, Cd could also be coating mineral particles. Since Cd and OM would have the same affinity to mineral, the correlation would be high, however sorption to mineral particles would be the governing factor.

Croue et al. (1999), suggested that sugars (polysaccharides) were represented in the chromatograph as furans and furfurals. Results showed that polysaccharide products seemed to govern the Cd distribution, due to high correlation factors (i.e. 0.98 and 0.97) between Cd distribution and polysaccharides. The amount of polysaccharides was in direct relation with the amount of OM. The percent of OM decreased with depth, going from 36.1% for OAe, to 21.4% for AEv, and finally to 9.9 for BE. This resulted in a decrease of sorbed cadmium with depth.

It was assumed that the dissolved materials were available for transport. The data suggested that streams, groundwater, and springs of the boreal watershed CPCRW have the potential to mobilize the heavy metal, cadmium.

I believe that a pH isotherm to find the real fixed cadmium would be important to run. pH being a variable and a key factor (Alloway, et al, 1990) more study should be done to see how it influenced the Cd sorption during the course of a year.

In the particle size separation process, a sample could be further filtered at 0.1μm. The particulates (0.45-0.1μm) are colloidals, below 0.1μm the particulates are considered dissolved. The water passing through this filter (i.e. 0.1μm) is drinking water. Therefore, Cd concentration should be determined to be in accordance with the safe drinking water act (SDWA) for Alaska, 0.005mg/L (primary maximum contaminant level MCL). The FAO/WHO recommended a maximum tolerable intake of 70μg/day of Cd (Fassett D.W.).

In addition, it would be interesting to know what is happening between cadmium and macromolecules (2-100nm), and polyelectrolyte. Macromolecular compounds can possess a large number of complexing sites. This is the case for polysaccharides (Buffle J. 1990). Therefore it would be interesting to repeat the experiment for filter sizes 0.1μm-2nm. It would be also useful to further investigate the relationship between Cd mobility and polysaccharides.

The seasonal variation in true color, ultraviolet absorbance at 254 nanometers (UV_{254}), and DOC concentration for 6 different streams and 6 different springs were compared. The seasonal variation of the true color, UV_{254} and DOC showed two distinct groups. One with higher values occurring in the late summer, and the other with higher values in early summer. The research also showed that there was little difference between true color-UV_{254}-

DOC relationship between spring and stream samples, though streams carried more NOM than springs year round. However there was a significant difference in this relationship as a function of sample collection time (i.e. March, June, August).

Using pyrolysis-GC/MS, a suite of molecules was selected to look at changes in the molecular composition of DOM in CPCRW. There was a significant difference of the molecular composition of the DOM as function of season. The most pronounced difference was an abundance of nitriles and a lack of alkylbenzenes in the March pyrolyzates when compared to June and August samples. These results were expected since the nitriles are believed to be derived from proteins accumulating from microbial degradation of organics over the winter. The alkyl benzenes, believed to be derived from decomposing lignin-rich plant material, were more abundant in the summer when material from the surface runoff enters surface water bodies.

Results from this research suggest that the organic matter abundance and molecular composition change appreciably over the course of the year.

It would be useful to investigate further the differences in water characteristics of the Caribou Creek watershed and of the Little Poker Creek watershed. A difference in water characteristics was found, however, is it coming from different type of vegetation, area covered by permafrost, soil types, and/or water leaching through different type of canopy, different recharge area, different residence time?

Cd sorption seemed to be well correlated to OM in Chapter 1. The chemical composition of OM was changing with time in Chapter 2. In Chapter 3, OM was used as a natural tracer to determine hydrological connection and/or similar biological and physical processes

undergone by the water, to better understand the potential of Cd mobility in boreal watersheds.

The hypothesis was that the water appearing on discharge area (north-facing slopes) was derived from recharge area (infiltration at higher elevations on the south-facing slopes), which could be outside the boundaries of the watershed. This hypothesis was confirmed. However, the correlation was slightly less than expected, probably due to contamination of the water samples due to aufeis, lag in collection time, surface water, or/and intra flow.

It was also expected to find the water downstream to be well correlated with an up-stream or groundwater source in winter, and the water downstream to be less correlated to groundwater source during the summer, due to an increasing amount of NOM in the stream. This was once again verified, for example, SB spring was correlated to Caribou Creek stream by a correlation coefficient equal to 0.73 in March and 0.13 in June.

In addition, the results suggested that the organic matter chemistry of the Little Poker Creek watershed's springs changed less than the organic matter chemistry of the Caribou Creek watershed's springs between 2000 and 2001.

The residence time of the water underground was determined to be one to three decades by CFCs and tritium analysis (Yoshikawa et al., 2002). Therefore natural tracers were used for the study. However the residence time of C3 sp and CB sp seems to be shorter (due to a strong identity, see relative abundance of compounds). So maybe artificial tracers could be used to check the residence time of the water in the ground.

The hypothesis that a large amount of water would be integrating the Caribou Creek stream around the collapsed pingo area, due to a fault, carrying the pingo spring water should be checked.

Finally, water samples of Caribou Creek and Little Poker Creek could be collected just before their intersection to allow an accurate analysis and comparison with CJ stream, and to allow a better correlation with up-streams samples.

Polysaccharide products seemed to be in direct relation to the sorption of Cd. Organic matter, being rich in polysaccharides, was thus well correlated to Cd distribution in the soil at different particles size as well as dissolved materials. It was assumed that the dissolved materials were available for transport. The data suggested that streams, groundwater, and artesian springs of the boreal watershed CPCRW have the potential to mobilize the heavy metal, cadmium. However, the organic matter abundance and molecular composition changed appreciably over the course of the year. In addition, the relative abundance of furfural (polysaccharide) seemed to decrease in summer (Figure 2.6). Therefore, the research suggested that Cd, as dissolved materials, has the potential to be transported by different water sources (principally streams; streams carrying more OM than springs), and in a larger amount in winter versus summer. In a further study, it would be important to determine the flux of cadmium that can be transported in the winter versus the summer, but also to see how the global warming would affect these fluxes.

As a last suggestion for further study, what is the fate of cadmium when arriving to the ocean? What is its impact on the ecological system? Would it be transported further than the river plume since it has been transported in dissolved and in particles? Would it enter the food chain?

LITERATURE CITED

1- Adriano D.C. 1986. Trace elements in the terrestrial environment. Spring-Verlag, New York.

2- Alloway B.J., Environmental Science, Queen Mary and Westfield College, University of London, " Heavy Metals in Soils", John Wiley & sons, Inc, 1990

3- Alloway B.J. 1990. cadmium.p.100-124. In B.J. Alloway (ed.) Heavy metals in soils. John Wiley and sons, New York

4- Beaulieu S. (2000). *Importance of benthic-pelagic coupling in the ocean carbon cycle.* Applied Ocean Physics and Engineering Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543. http://www.whoi.edu/science/AOPE/cofdl/stace/OCTET_EDOCC.htm

5- Beget Jim (2002) Geology Dept, tephrochonolgy specialist, personal communication

6- Bennett, B.G., *Exposure Commitment Assessments of environmental pollutants* Vol 1., No1. MARC, London (1981)

7- Biddappa, C.C., Chino, M. and Kumazawa, K. *Plant and soil* 66 (1982) 299-316

8- Blom, E. B. *Sorption of Cadmium by soils* Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire (1974) GB 2401 C76 no 320 c.2

9- Boul, S.W., F.D. Hole, R.J. McCraken, and R.J. Southard (1997). *Soil Genesis and classification,* 4th ed (Ames, Iowa; Iowa state University press)

10- Brady N.C., Ray R. Weil (1999) The nature and properties of soils. *2-18 The soil profile* P65-69. 12th ed Prentice hall

11- Brummer, G., K.G. Tiller, U. Herms, and P.M. Clayton. 1983.*Adsorption-desorption and/or precipitation-dissolution processes of Zinc in soils.* Geoderma 31:337-354

12- Buffle J., *The components of aquatic systems and their reactivity; Complexation reactions in aquatic systems*, Ellis Hordwood (1990), 16-89, 21.

1- Buffle J., *Complexation reactions in aquatic systems; Distinction between aquagenic and pedogenic NOM,* Ellis Hordwood (1990), 122-132

13- Buffle J. and Deladoey P. 1982 *Schweiz. Z. Hydrol.* 44, 363

14- Chapman, R.M, F.R. Weber, and B. Taber. 1971. Preliminary geologic map of Livengood quadrangle. U.S. Geological Survey. Open File Report 483. scale 1:250,000

15- Christensen, T.H., Water, Air & Soil Pollution 21, 1984, 105-114

16- Clair N. Sawyer, Perry L. McCarty, Gene F. Parkin. *Chemistry for Environmental Engineering; Basic concepts from General Chemistry,* Mc Graw-Hill series in water resources and environmental engineering, 1994, 36-38.

17- Clesceri L.S., Greenberg A.E., and Deaton A.D., eds., 1998. *Standard Methods for the Examination of Water and Wastewater, 20th ed.* American Public Health Association, American Water Works Association, Water Environment Federation, Washington, D.C.

18- Collins, C.M., 1986. *The installation of long term ground temperature monitoring sites in the Caribou-Poker Creeks Research Watershed.* Technical note. NH: U.S. Army Cold Region Research and Engineering Laboratory. P. 28

19- Croue, J-P., Debroux, J-F, Amy G.L. Aiken, G.R. and Leenheer J.A., 1999. *NOM: structural characteristics and reactive properties; Formation and Control of Disinfection By-Products in Drinking Water,* P.C. Singer, ed/ American Water Works Association, Denver CO, 65-89

20- David W. Rutherford, Cary T. Chiou. *Effect of water in Soil Organic Matter (SOM) Composition on the Partition of Organic Compounds,* U.S. Geological Survey, Environmental Sci. Technol. 1992, 26, 965-970.

21- Fanning, D.S., and C.B. Fanning 1989 *Soil: Morphology, Genesis, and classification* (New York, Jhon Wiley and Sons)

22- Fassett, D.W., *Metals in the Environment* ed. Waldron, H.A. Academic Press, London (1980), 61-110

23- Fedeler B., 2001 University of Minnesota Duluth, Natural Resources Research Institute http://wow.nrri.umn.edu/wow/teacher/conduct/teaching.html

24- Fleischer, M., Sarofim, A.F., Fassett, D.W., Hammond, P.Shacklette, H.T., Nisbet, I.C.T. and Epstein, S., *Environ. Health Perspect.* 7 (1974), 253-323

25- Flick, D.F., H.F. Kraybill, and J.M. Dimitroff. 1971. Toxic effects of cadmium: A review. Environ. Res. 4:71-85

26- Forbes, R.B., and Weber, R.R., 1982: *Bedrock geologic map of Fairbanks mining district*, Alaska. Alaska Division of Geological and Geophysical Surveys, open file report 170.

27- Haugen, R.K.; Slaughter, C.W.; Howe, K.E.; Dingman, S.L. 1982. *Hydrology and climatology of the Caribou-Poker Creeks Research Watershed, Alaska.* CRREL Rep. 82-26. Hanover, NH: U.S. Army Cold Regions Research and Engineering Laboratory. 42 p.

28- Hutton, M. *Cadmium in the European community,* MARC Rep. No. 2., London (1982)

29- Lamy I., Bourgeois S., and Bermond A. 1993. *Soil cadmium Mobility as a Consequence of Sewage Sludge Disposal.* Environ. Qual. 22:731-737

30- Lawson, D.E., Arcone, S.A., Collins, C.M., 1991. *Geophysical investigations of an anomalous unfrozen zone, Caribou Peak, Alaska.* CRREL Report Number 91-17. Hanover, NH: U.S. Army Cold Region Research and Engineering Laboratory.P.24

31- Leya T., Müller T., Ling H. U., Fuhr G. (2000) *Taxonomy and biophysical properties of cryophilic microalgae and their environmental factors in northwest Spitsbergen, Svalbard.* 57th Eastern Snow Conference, Syracuse, New York, USA.

32- Mayer L. M. (1994a) Surface area control of organic carbon accumulation in continental shelf sediments. Geochim. Cosmochim. Acta 58, 1271-1284.

33- Mayer L. M. (1994b) Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. Chem. Geol. 114, 347-363.

34- McGrath, S.P., in *Trace Substances in Environmental Health* 20 (1986) 242-252

35- Naidu R. ; Kookana, R.S Sumner. M.E. 1997. *Cadmium sorption and transport in variable charge soils.* Journal of Environmental quality v. 26 (May/June 1997) P.602-617

36- Naidu R., M.E. Sumner, and R.D. Harter. 1997. Sorption of heavy metals in strongly weathered soils: An overview. J. Environ. Geochem. Health (In press)

37- Page, AS.L., Chang, A.C., and Mohamed El-Amamy, in *Lead, Mercury, Cadmium and arsenic in the environment* SCOPE 31, eds. Hutchinson, T.C. and Meena, K.M. John Wiley, Chister (1987), 119-146

38- Pickering, W., *Cadmium in the environment. Part 1 Ecological Cycling,* ed Nriagu, J.C John Wiley, New York (1980), 365-397

39- Ray, S.R. 1988. Physical and chemical characteristics of headwater streams at Caribou-Poker Creeks Research Watershed, Alaska. Master's thesis, University of Alaska. Fairbanks, Alaska. 172 pp.

40- Rieger, S.; Furbush, C.E.; Schoephorster, D.B.; Summerfield, H., Jr.; Geiger, L.G. 1972. *Soils of the Caribou-Poker Creeks Research Watershed.* Tech. Rep. 236. Hanover, NH: U.S. Army Cold Regions Research and Engineering Laboratory. 11 p

41- Sánchez-Martín M.J. and Sánchez-Camazano M. 1993. Adsorption and Mobility of Cadmium in Natural, Uncultivated Soils. Environ. Qual. 22:737-742

42- Sposito, G. and Page, A.L., in *Metal Ions in Biological Systems,* ed.Sigel, H. Marcel Dekker, New York (1984), 287-332

43- Stevenson, F.J., 1994: *Soil lipids.* P169. Humus chemistry, Genesis, Composition, Reactions. Jhon Wiley & Sons, Inc

44- Street, J., Lindsay, W.L. and Sabey, B.R., J. *Environ. Qual.* 6 (1977), 72-77

45- Suen-Zone L., H. E. Allen, D. L. Sparks, P. F. Sanders, and W. M. Peijnenburg. 1996. Predicting Soil-Water Partition Coefficient for Cadmium. Environ. Sci. Techn. 30, 3418-3424

46- Tiller K.G. 1989. Heavy metals in soils and their environmental significance. Adv. Soil Sci. 9:113-142

47- Tills, A.R. and Alloway, B.J. *J. Soil. Sci* 34 (1983), 769-781

48- Webster, J.R., and J.L. Meyer. 1997. *Stream organic matter budgets.* Journal of the North American Benthological Society 16:3-161

2- White D.M. and Beyer L., 1999. *Pyrolysis-GC/MS and GC/FID of three Antarctic soils*, Journal of Analytical and Applied Pyrolysis, Vol. 50, p63-76

49- White D.M. Yoshikawa K., and Garland S. 2002. *Use of dissolved organic matter to support hydrologic investigations in a permafrost dominated watershed.* Cold Regions Science and Technology. Accepted for publication.

50- Yoshikawa K., D. White, L. Hinzman, D. Goering, K. Petrone, and W. Bolton. Institute of Northern Engineering, University of Alaska Fairbanks, USA (2002); N. Ishikawa, Institute of Low Temperature Science, Hokkaido University, Japan. *Water in permafrost; case study of aufeis and pingo hydrology in discontinuous permafrost.* Accepted for publication

51- Zakaria A. M., *Removal of cadmium and manganese by a non-toxic strain of the freshwater cyanobacterium Gloeothece magna,* (2001) Water Research, Vol. 35 (18) 4405-4409.